Coordination Chemistry

DOI: 10.1002/anie.200900981

A Rhenium Tricarbonyl 4′-Oxo-terpy Trimer as a Luminescent Molecular Vessel with a Removable Silver Stopper**

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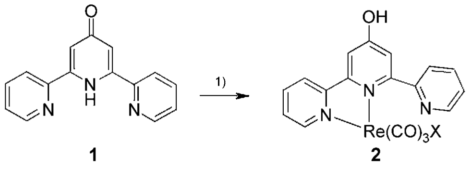
One of the great challenges for the synthetic chemist is the preparation of large, hollow, molecular species capable of hosting smaller molecules. In contrast to solid-state materials, which have no true existence in solution, there are only a very small number of truly discrete families of molecular species that provide a shell enclosing a void, such as calixarenes,[1a] cyclodextrins,[1b] and cucurbiturils.[1c] In the field of coordination chemistry, this area has been dominated by the self-assembly of cage complexes.[1d] Multidentate ligands that may bind more than one metal center provide a route to cage complexes,[1e–i] and the use of preformed complexes with additional binding sites (complex-as-ligand approach) has led to a variety of coordination networks with a range of complex topologies, including examples of cage complexes appropriate for host–guest applications.[2] Coordination complexes containing cylindrical or psuedo-cylindrical cavities analogous to cyclodextrins or calixarenes are, however, very rare, with very few examples of metallacalixarenes, in which arene ligands mimic calixarene walls.[3] These species potentially offer more modes of binding than the organic analogues: both organic-based ligand–guest interactions similar to those in pure organic systems, and contributions from metal–guest or charge–guest interactions. Furthermore, coordination complexes acting as hosts may, with judicious choice of metal and ligand, be capable of responding to the presence of the guest by modulation of a detectable property, such as luminescence. Amongst the most widely studied luminescent metal complexes are the rhenium tricarbonyl bisimine cations $[\mathrm{Re(CO)_3(bisim)X}]^+$ (bisim = 2,2′-bipyridine or derivative thereof; X = pyridine or derivative) owing to their high quantum yields, long luminescence lifetimes, and large Stokes shifts arising from emission from a ^{3}MLCT excited state.[4] Recently these species have been applied in the fluorescence microscopy imaging of cells,[5] and many have been proposed as sensors in the past.[6] No examples of rhenium metallacalixarenes, and indeed no ^{3}MLCT emissive metallacalixarenes have been reported to date, and no rational design for such species exists.[3] Herein we report the development of a luminescent rhenium bisimine-based cylindrical trimer synthesized by the complex-as-ligand approach: the cavity has the correct dimensions for hosting linear diatomics, and a pendant tripyridine unit can bind metal ions, closing one end of the cylinder to form a cup and simultaneously triggering a modulation of the luminescence of the core trimer.

The reaction of **1**[2c] with rhenium pentacarbonyl bromide or chloride gave the expected product [Re(4′oxo-η^2-terpy)(CO)$_3$]X **2** (terpy = 2,2′:6′,2′′-terpyridyl, X = Cl, Br), in which one of the terminal pyridine rings is uncoordinated[7] and the central ring has tautomerized to the 4-hydroxypyridine form (Scheme 1). Typically, halide abstraction activates the rhenium tricarbonyl bisimine complexes, allowing attack by pyridines or other ligands, which could lead to a range of interesting oligomers if the pendent pyridine or the oxo unit then linked rhenium cores (Figure 1). Abstraction of the halide from **2** with silver tetrafluoroborate in acetonitrile gave [Re(4′oxo-η^2-terpy)(CO)$_3$(MeCN)]BF$_4$ **3** (Scheme 2). This behavior, although typical in simple examples of these systems, was unexpected: such acetonitrile complexes are reactive, and it could be expected that upon halide abstraction, either the pendant pyridine or hydroxy group would compete with (or subsequently displace) acetonitrile to give a higher nuclearity complex. The stability of **3** may be explained by the ability of the ligand to lose a proton and generate the neutral species, which could be expected to be of lower reactivity than the cationic acetonitrile complexes derived



Scheme 1. Coordination of bispyridylpyridone **1** to rhenium pentacarbonyl halides. Conditions: 1) [Re(CO)$_5$X], toluene, reflux; X = Cl, Br.

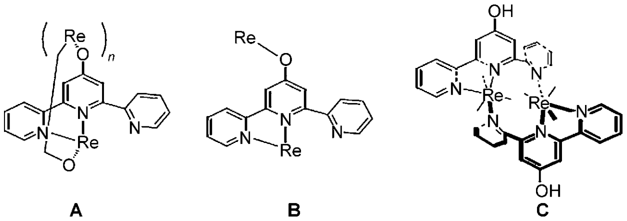


Figure 1. Possible structures from oligomerization of rhenium terpy: A cyclization, B chain formation, C dimerization.

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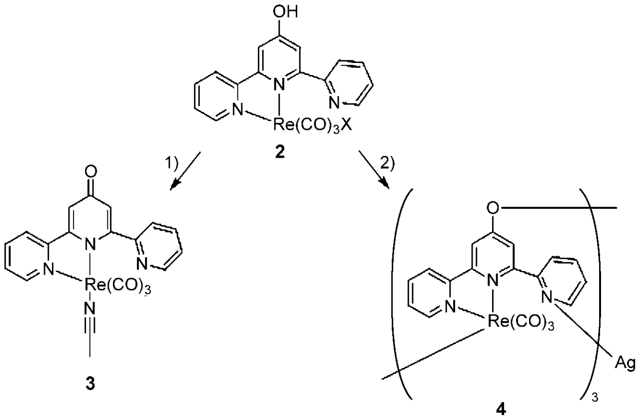
[**] We thank the EPSRC National Mass Spectrometry Service Centre, Swansea, for HRMS. Terpy = 2,2′:6′,2′′-terpyridyl.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900981.



Scheme 2. Abstraction of halides from complex **2**. Conditions: 1) 1 equiv $AgBF_4$, MeCN; 2) 3 equiv $AgBF_4$, MeCN. The oxygen atom in **4** coordinates to a neighboring rhenium atom.

from other bisimines. Although this seemed an unpromising route to form oligomeric complexes, serendipity delivered a route to a unique architecture, which becomes available when an excess of silver was used in the halide abstraction (Scheme 2). Treatment of **2** with three equivalents of silver tetrafluoroborate led to a product that was shown by X-ray crystallography to be the trimeric macrocyclic cation $[\{(\eta^{Re}\text{-}4'\text{-oxo-}1,1'\text{-}\eta^{Re}\text{-}1''\text{-}\eta^{Ag}\text{-terpy})Re(CO)_3\}_3Ag]^+$ (**4**; Figure 2 a).

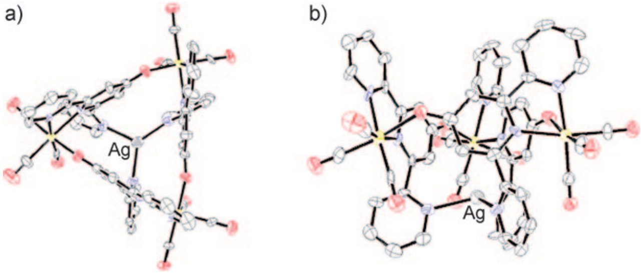


Figure 2. ORTEP diagram of cation **4**. Ellipsoids set at 50% probability; hydrogen atoms excluded for clarity. Ag gray, Re yellow, O red, N blue.

Three molecules of the rhenium terpyridine unit **2** have cyclotrimerized through the 4′-oxygen, forming a pseudo-cylindrical species with the two bound pyridine groups forming the walls of a triangular cavity; the remaining pendant pyridine of each unit binds to a single silver ion which caps one end of the cylinder (Figure 2 b). The charge of this cation in the crystal is balanced by a disordered mixture of halide and tetrafluoroborate anions. The average of the C-O-Re angles of the oxopyridine bridges between each rhenium complexes is 138.5°, and of the N-Re-O angles is 80.1°. These terpyridine units form the approximately planar sides between rhenium corners of a triangular channel, which is open at one end and capped at the other by the silver ion. The dimensions of this molecular cavity are described by a triangle of approximately equilateral geometry, with sides averaging to 8.0 Å and an inscribed circle with an average diameter of 4.6 Å. The void circle of the cup is maintained throughout its length; the rim of the cup is formed from the aromatic rings of one of the coordinated pyridines, and is approximately 10 Å from the silver ion that forms the cap at the far end (Figure 2). The three silver-coordinated pyridine groups form a propeller-shaped stoppage with average nitrogen–silver bond lengths of 2.27 Å. This value is at the shorter end of observed silver–nitrogen bonds in silver complexes, which range from 2.29–2.58 Å.[8] Rather than arising as a result of a particularly strong silver–nitrogen bond, this distance may reflect the intrinsic geometry of the trimer in which the pyridines are preorganized into this arrangement. The other bond lengths and angles are typical for rhenium–pyridine and rhenium–carbonyl structures. The cavity is of insufficient radius to easily allow a free flow of saturated hydrocarbon (internal volume of approximately 150 $Å^3$); however, **4** could well act as a host for monoatomic ions or linear di- or triatomic ions and molecules, and is a prototype of a new class of metallacalixarenes (Figure 3). Although the silver ion completes the cavity by blocking one end of the cylinder, the silver-free tube or pipe equivalent is also of interest, as this could not only act as a host, but the three pendant pyridines are preorganized to chelate metal ions. Such ions would not only potentially sense the presence of such ions, but, by incorporating other metals, could act as a starting material for heterometallic analogues of **4**.

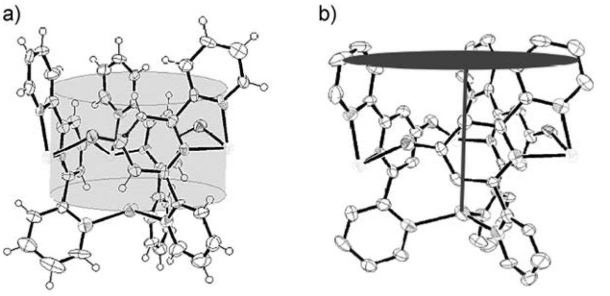


Figure 3. Dimensions and cavities of cation **4** (carbonyl groups omitted): a) Shaded region shows the void space with a diameter of 1.6 Å; b) vertical line indicates the distance (9.7 Å) of the silver ion to the rim (gray disk).

It was observed that stoichiometric silver halide abstraction from **2** gives **3**, whereas an excess of silver is required to form **4**. This result suggests that the formation of **4** requires preorganization of **3** by templating around a silver ion, which was reinforced by attempts to trimerize **3** by thermal loss of acetonitrile (in refluxing toluene), which proved unsuccessful even after several days. Attempts to remove the silver ion from **4** were equally unsuccessful. Treatment of **4** with a range of argentophilic anions (Cl^-, F^-, SCN^-, I^-, S^{2-}) in the hope of extracting the silver ion, or with cations which could be expected to compete for pyridine binding (Cu^I, Cu^{II}, Zn^{II}), each resulted in no reaction under mild conditions and to decomposition of the trimer under forcing conditions. Happily, although these attempts to remove the silver stopper by chemical reactions failed, the silver ion could be removed photochemically, and the silver-free trimer $[\{(\eta\text{-}4'\text{-oxo-}\eta\text{-}2,2'\text{-terpy})Re(CO)_3\}_3]$ **5** was eventually accessed from photolytic loss of silver from a solution of **4**. It was discovered that upon standing in sunlight, crystals grew from a solution of **4** that were shown by X-ray crystallography to be **5**, and subsequent conversion of **4** into **5** was accomplished upon irradiation of a solution of **4** with a 405 nm laser, along with the precipitation of silver. The removal of this ion is reversible however: upon treatment of **5** with silver tetrafluoroborate, **4** is immediately formed, thus the stopper of the vessel can be removed and subsequently replaced.

The X-ray crystal structure of **5** (Figure 4) shows that this neutral species has an analogous molecular geometry to **4**, with an essentially identical triangular channel of the same dimensions as **4**; however, the silver ion capping one end of the channel is missing. Two of the pendant pyridine nitrogen atoms point into the cavity of the macrocycle (Figure 4b). However, as shown by solution spectroscopic studies, this conformation is not unique; the pyridine groups were found to be equivalent owing to free rotation, rendering them able to bind ions.

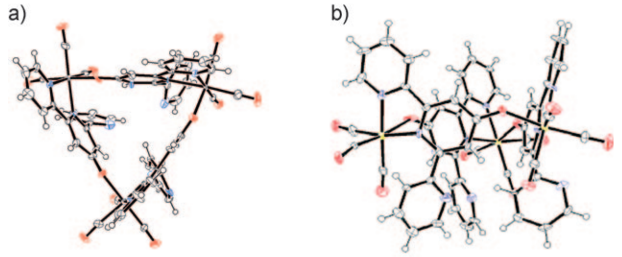


Figure 4. Molecular structure of **5**. Ellipsoids set at 50% probability; solvent molecule (MeCN) excluded. Re yellow, O red, N blue.

Both of these macrocyclic species retain the useful photophysical properties which are associated with rhenium tricarbonyl bisimine species. Complexes **4** and **5** have electronic spectra containing broad absorption bands at 348 nm and 352 nm, respectively, with extinction coefficients of about 14000 $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, which appear as shoulders on much stronger higher-energy bands. These lowest energy absorptions are assigned by reference to previous studies[4] as being of dπ–π^* ^{1}MLCT in origin, with the higher-energy bands being related to ligand-centered π–π^* transitions, and are typical in wavelength and absorption of such transitions. Both **4** and **5** are emissive, and their luminescent properties were studied and are summarized in Table 1. Both compounds show luminescence typical of rhenium bisimine species, with excitation maxima in the region of 350–380 nm and emission maxima at about 550–570 nm. The luminescence lifetimes τ of **4** and **5** were measured using TCSPC methods (Table 1) and both fall in the 20 ns region, which is short compared to the popular rhenium tricarbonyl bisimine cations, but typical of similar neutral species.[4] The luminescence quantum yields Φ of **4** and **5** were measured and are in the region of 0.1–0.2% (Table 1). Again, these quantum yields are low in comparison to cationic species, but are typical for neutral analogues. The photophysical properties taken together, including the large Stokes shifts (ca. 10000 cm^{-1}), broad excitation and emission bands, and lifetimes, are all characteristic of rhenium bisimine phosphorescence, demonstrating that these macrocyclic species display ^{3}MLCT emission. Although the luminescence properties of **4** and **5** are overall quite similar to each other, and each typical of such neutral rhenium bisimines, there are characteristic differences between the emissive properties of the two species that bode well for the application of such species in ion sensing. An overlay of the excitation and emission spectra of isoabsorbing **4** and **5** (Figure 5) demonstrates the changes in the photophysical properties that are induced by the binding of the silver ion in **4**. The form of the excitation spectrum changes and the emission maximum shifts from 557 nm to 566 nm. Additionally, the higher quantum yield of **5** compared to **4** indicates the effect of the silver ion on the luminescence of the macrocyclic core. Whereas **4** is unstable to irradiation, losing silver to form **5**, this latter species appears to be photostable, at least to visible light. Multiple experiments showed no evidence of any decomposition of **5** or of other species being formed upon 10 mW irradiation for 24 h at 405 nm.

Table 1: Luminescent properties of complexes **4** and **5**.

	UV λ_{max} [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$])	Excitation λ_{max} [nm]	Emission λ_{max} [nm]	Lifetime τ [ns]	Quantum yield Φ
4	348 (13300)	361	566	20	0.0015
5	352 (14900)	365	557	22	0.0019

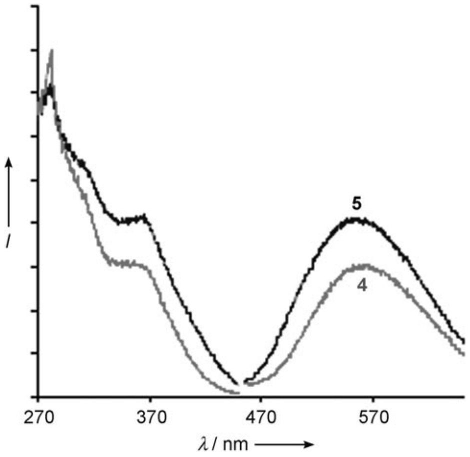


Figure 5. Excitation and emission spectra of **4** and **5**.

These unique structures and useful luminescent properties indicate that complexes **4** and **5** show great promise as macromolecular species for applications in host–guest chemistry and sensing.

Experimental Section

Details of the synthesis and characterization of **2**–**5** are given in the Supporting Information. CCDC 721022 (**4**) and CCDC 721023 (**5**) 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.

Crystal data for **4**: $C_{54}H_{30}AgBClF_4N_9O_{12}Re_3$, $M_r = 1785.60$, yellow needle, $0.20 \times 0.20 \times 0.20$ mm^3, monoclinic, $P2_1/c$, $a = 13.468(3)$, $b = 38.005(8)$, $c = 13.015(3)$ Å, $\beta = 109.55(3)°$, $V = 6278(2)$ Å^3, $Z = 4$, $\rho_{cald} = 1.889$ g cm^{-3}, $\mu = 6.191$ mm^{-1}. KappaCCD, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 150(2)$ K, $2\theta_{max} = 54.9°$, 40144 reflections, 12832 unique ($R_{int} = 0.0977$). Final $GooF = 1.039$, $R1 = 0.0748$, $wR2 = 0.1894$.

Crystal data for **5**: $C_{55}H_{33}N_{11}O_{12}Re_3$, $M_r = 1598.52$, yellow needle, $0.24 \times 0.14 \times 0.10$ mm^3, triclinic, $P\bar{1}$, $a = 12.8910(2)$, $b = 14.9140(2)$, $c = 15.0690(3)$ Å, $\alpha = 75.9180(10)$, $\beta = 89.4410(10)$, $\gamma = 78.1010(10)°$, $V = 2747.18(8)$ Å^3, $Z = 2$, $\rho_{cald} = 1.932$ g cm^{-3}, $\mu = 6.666$ mm^{-1}. KappaCCD, MoKα radiation, $\lambda = 0.71073$ Å, $T = 293(2$ K, $2\theta_{max} = 55.0°$, 18753 reflections, 12529 unique ($R_{int} = 0.0401$). Final $GooF = 1.151$, $R1 = 0.0879$, $wR2 = 0.2221$.

Received: February 19, 2009
Revised: April 8, 2009

Keywords: host–guest chemistry · luminescence · metallacycles · molecular vessels · rhenium

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