Hosting a Radioactive Guest: Binding of $^{99}TcO_4^-$ by a Metalated Cyclotriveratrylene

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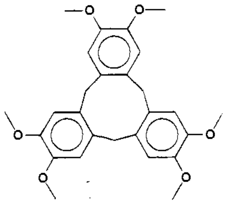
Cyclotriveratrylene (CTV, **1**) is the readily available trimeric macrocycle derived from the acid-catalyzed condensation of formaldehyde with veratrole.[1] Its capacity to form solid state inclusion compounds is well documented.[2] In these materials, guest molecules generally occupy voids in the crystalline lattice which arise as a consequence of the columnar stacking of the saucer-shaped CTV units,[2a] although recently we have reported a fullerene inclusion complex of CTV which is of the intrabowl "ball and socket" variety.[2b]



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Previous work has demonstrated that the complexation of the aromatic rings of various calix[*n*]arenes[3] to transition metal-containing moieties results in significant changes in the reactivity[3a,b] and the host–guest properties[3c,d] of the macrocycle. In particular, the buildup of positive charge upon the metal-coordinated aromatic rings of $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_4(\eta^6{:}\eta^6{:}\eta^6{:}\eta^6\text{-calix[4]arene} - 2H)]^{6+}$ results in the deep inclusion of one of the tetrafluoroborate anions within the ostensibly hydrophobic cavity of the host.[3c] Similar intrabowl anion complexation properties were anticipated for metalated CTV derivatives, and indeed the X-ray crystal structure of the trimetallic host complex $[\{Ru(p\text{-}MeC_6H_4CHMe_2)\}_3CTV][BF_4]_6$ (**2**) demonstrates the inclusion of one of the tetrafluoroborate anions within the wide, shallow cavity of the host.[2b]

The supramolecular chemistry of anions[4] is a relatively unexplored, though increasingly topical, field in comparison with that of cations[5] and neutral molecules.[6] The noncovalent binding of anions is of considerable interest in the fields of molecular recognition and development of synthetic enzyme analogues or in the context of removal of environmental contaminants such as phosphate[7] or the radioactive $^{99}TcO_4^-$ anion[8] produced in the nuclear fuel cycle. Although the radiotoxicity of ^{99}Tc is relatively low, its behavior in the environment is of considerable concern as a consequence of its long half-life of 2.13×10^5 years. In this Communication, we report the synthesis and anion binding properties of the dimetalated CTV derivative $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-CTV})]^{4+}$ (**3**) with $CF_3SO_3^-$, ReO_4^-, and TcO_4^-. Although the redox behavior of Tc is markedly different from that of Re, the ReO_4^- anion makes an excellent structural model for TcO_4^- as a consequence of their similar size[9] and topology. The results are directly linked to the MO_4^- (M = Re, Tc) binding properties of the host observed by radiotracer studies using the ^{188}Re and ^{99m}Tc isotopes.

Treatment of the ruthenium complex $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)Cl(\mu\text{-}Cl)\}_2]$ (**4**) with $Ag[CF_3SO_3]$ in acetone, followed by refluxing with 1 equiv of CTV in neat CF_3CO_2H, resulted in the clean formation of the bimetallic complex $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-CTV})][CF_3SO_3]_4$ (**3a**). Crystals of composition **3a**$\cdot H_2O$ are afforded in an overall yield of 90% by allowing ether vapor to diffuse into a nitromethane solution of the product. The formulation of **3a** was confirmed by NMR spectroscopy[10] and single crystal X-ray structure determination[11] as well as by IR spectroscopy, FAB-MS, and analytical data. The ^1H NMR spectrum of **3a** shows unambiguously that only two faces of the CTV unit are coordinated to metal centers, and is consistent with the spectrum observed for the monometalated derivative.[2b] The ^{19}F NMR spectrum[14] of **3a** also demonstrates the presence of $CF_3SO_3^-$ anions.

The X-ray crystal structure of **3a**$\cdot H_2O$ demonstrates that the cation adopts the conventional shallow bowl-shaped conformation (Figure 1), with an intracentroid separation of 4.70 Å between metalated aromatic rings. This is relatively short in comparison to 4.81 Å as the average of the other two intracentroid separations and values of up to 4.96 Å in the free ligand.[2a,c–g] More importantly, one of the $CF_3SO_3^-$ anions is deeply embedded within the bowl-shaped CTV cavity. The negatively charged SO_3^- head group is oriented predominantly toward one of the metalated rings, while the hydrophobic CF_3 tail is situated in the more hydrophobic region of the cavity,

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(10) ^1H NMR data ($NO_2Me\text{-}d_3$, 250 MHz, 22 °C, δ/ppm, J/Hz) for **3a**: δ 7.75 (s, 2H, coord CTV ring), 7.56 (s, 2H, coord CTV ring), 7.17 (s, 2H, uncoord CTV ring), 7.03, 6.99 (AB, 4H, $^3J = 7.1$, cymene), 4.65, 4.13 (AB, 2H, $^2J = 13.6$, proximal CH_2), 4.61, 3.88 (AB, 4H, $^2J = 14.1$, distal CH_2), 4.22 (s, 12H, OMe), 3.86 (s, 6H, OMe), 3.00 (sp, 1H, $^3J = 7.0$, C*H*Me$_2$), 2.61 (s, 6H, Me), 1.39 (d, 12H, $^3J = 6.9$, CH*Me*$_2$). **3b**: δ 7.67 (s, 2H, coord CTV ring), 7.47 (s, 2H, coord CTV ring), 7.13 (s, 2H, uncoord CTV ring), 7.00 (m, 4H, cymene), 4.67, 4.03 (AB, 2H, $^2J = 13.6$, proximal CH_2), 4.61, 3.83 (AB, 4H, $^2J = 14.1$, distal CH_2), 4.25 (s, 6H, OMe), 4.21 (s, 6H, OMe), 3.86 (s, 6H, OMe), 2.99 (sp, 1H, $^3J = 6.9$, C*H*Me$_2$), 2.61 (s, 6H, Me), 1.39 (d, 12H, $^3J = 6.9$, CH*Me*$_2$).

(11) Crystal data (293 K, Enraf-Nonius CAD4 diffractometer): $C_{47}H_{58}O_6Ru_2\cdot 4CF_3SO_3\cdot H_2O$, $M_r = 1535.41$, yellow plate, monoclinic, $P2_1/n$, $a = 9.537(4)$ Å, $b = 39.083(6)$ Å, $c = 17.855(8)$ Å, $\beta = 99.72(2)°$, $V = 6560(4)$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, μ(Mo Kα) = 6.87 cm^{-1}. Of 9725 data collected ($2\theta_{max} = 46°$), 9086 were independent and 6307 were judged observed [$I > 2\sigma(I)$]. The structure was solved by direct methods (SHELXS-86)[12] and completed using difference Fourier synthesis (SHELXL-93).[13] Final residual $wR_2 = 0.210$ for all data, corresponding to a conventional R factor of 0.056 based on observed reflections.

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(14) ^{19}F NMR data ($NO_2Me\text{-}d_3$, 235 MHz, 22 °C, δ/ppm, CCl_3F as internal standard) for **3a**: δ −78.00 (s, $CF_3SO_3^-$). **3b**: δ −78.01 (s, $CF_3SO_3^-$). $AgCF_3SO_3$: δ −77.70 (s, CF_3SO_3).

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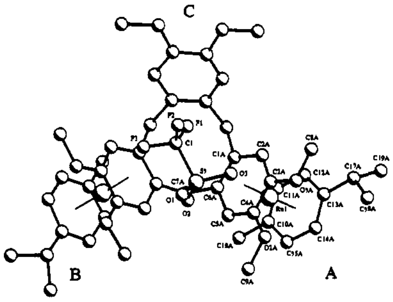

Figure 1. X-ray crystal structure of the host cation $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-}CTV)]^{4+}$ in **3a** along with the included $CF_3SO_3^-$ anion. The negatively charged SO_3 portion of the guest anion is oriented toward the metalated rings.

near the nonmetalated ring. Two of the oxygen atoms are approximately at the upper rim of the cavity, with the closest anion−cation contacts of O12···C2B = 2.95 Å and O12···C5A = 3.02 Å, suggesting tight binding of the guest. All of the other anions in the lattice exhibit longer anion−cation contacts, with the closest (3.10 Å) involving one of the *p*-cymene ligands. Furthermore, the tight binding of the anionic guest is highlighted by the relatively small crystallographic thermal parameters of its atoms; this is in contrast to the free lattice anions which commonly exhibit comparatively large thermal parameters as a result of dynamic disorder or high thermal motion.

Dissolution of crystals of $\mathbf{3a}\cdot H_2O$ in nitromethane, together with a 2-fold excess of $[NBu_4][ReO_4]$, followed by slow vapor diffusion of diethyl ether into the solution, results in the isolation of crystals of the mixed salt $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-}CTV)][CF_3SO_3][ReO_4]_3\cdot NO_2Me$ ($\mathbf{3b}\cdot NO_2Me$). The ^1H NMR spectrum of **3b**[10] is similar to that of **3a** and again exhibits the three singlet pattern for the aromatic protons of the CTV residue. The IR spectrum of **3b**, however, displays absorption at 900 cm^{-1}, assigned to the ReO_4^- anion (*cf.* 907 cm^{-1} for $[NBu_4][ReO_4]$ and 920 cm^{-1} for $K[ReO_4]$[15]).

The X-ray crystal structure of **3b**[16] shows clearly that three of the $CF_3SO_3^-$ anions have been replaced by ReO_4^- anions, including the one within the macrocycle cavity. The single remaining $CF_3SO_3^-$ anion could not be well characterized crystallographically due to extreme disorder but is evidenced by the ^{19}F NMR spectrum (δ −78.01 ppm) of the complex.[14] All of the ReO_4^- anions were refined with idealized tetrahedral geometries as a consequence of the paucity of observed data and poor crystal quality, but the locations of the anions are clearly apparent. The one within the cavity is situated so that three of the oxygen atoms are approximately at the upper rim of the cavity and one is pointing directly out. Notably, the anion is not centered within the cavity but rather has been drawn toward the two metalated rings of the CTV portion (Figure 2), with Re···centroid distances of 4.06, 3.96, and 4.51 Å to metalated rings A, B, and nonmetalated ring C, respectively. The closest anion−cation O···C intermolecular contacts involving the three lower oxygens of the embedded anion range from 2.96 to 3.10 Å.

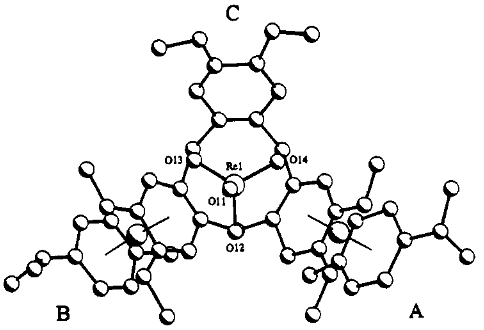

Figure 2. X-ray crystal structure of the cation $[\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)\}_2(\eta^6{:}\eta^6\text{-}CTV)]^{4+}$ in **3b** along with the included ReO_4^- anion. Note the size complementarity and position of the anion.

Solution studies of perrhenate binding to **3** were performed by radiotracer studies using ^{188}Re and ^{99m}Tc as mimics for the higher concentration of nonradioactive ReO_4^-. A saline solution of ammonium perrhenate spiked with radiotracer was extracted with an equal volume of nitromethane containing an equimolar amount of **3a**. After vortexing and centrifugation, aliquots of each layer were counted for activity content. Results are reported as the percent activity in the nitromethane layer. A 3.25 mM saline solution of ReO_4^-, spiked with $^{188}ReO_4^-$, extracted with a 3.25 mM solution of **3a** in nitromethane produced 71% of the perrhenate in the nitromethane. A blank of nitromethane with no host produced only 7% in the nitromethane layer. The concentration of the anion was then lowered with respect to **3**, producing a similar percentage in nitromethane for 2:1, 5:1, 10:1, and 100:1 **3**:ReO_4^- ratios. Similar studies were carried out with ^{99m}Tc tracer and resulted in 84% activity in the nitromethane for the various concentrations of anion. The blank had 6% activity in the nitromethane. Control experiments involving tetrabutylammonium as the cationic "host" displayed significantly less partitioning of activity into the nitromethane layer and a large dependence on concentration. These studies suggest that **3** has a specific affinity for these tetrahedral guests over $CF_3SO_3^-$ and that it may even discriminate between TcO_4^- and ReO_4^-, due to either size or electronic differences. The perrhenate anion is commonly used as a nonradioactive analog for pertechnetate, yet these results suggest that there may be a significant difference between the chemistry of ReO_4^- and TcO_4^- in this case.

This study demonstrates that the rigid organometallic hosts based on CTV are of a suitable size to include large tetrahedral anions such as MO_4^- (M = Tc, Re). The close ion pairing of **3** with $CF_3SO_3^-$ and ReO_4^- is indicative of a marked host−guest affinity, while solution studies with both $^{188}ReO_4^-$ and $^{99m}TcO_4^-$ suggest a significant degree of selectivity for these anions over trifluoromethanesulfonate. It is suggested that such anion selectivity arises as a consequence of the rigidity of the host framework, which may even form a size basis for the selective complexation of TcO_4^- over ReO_4^-.

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Supporting Information Available: Crystallographic summary for **3a,b**, including tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and isotropic displacement parameters (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[16] Crystal data (293 K, Enraf-Nonius CAD4 diffractometer): $C_{47}H_{58}O_6Ru_2\cdot 3ReO_4\cdot CF_3SO_3\cdot NO_2Me$, $M_r = 1.96$ g cm^{-3}, yellow needle, monoclinic, *Pn*, $a = 9.408(3)$ Å, $b = 19.308(3)$ Å, $c = 17.952(4)$ Å, $\beta = 101.89(1)°$, $V = 3191(1)$ Å^3, $Z = 2$, $D_c = 1.958$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 6.24$ cm^{-1}. Of 6444 data collected ($2\theta_{max} = 50°$), 6318 were independent and 3869 were judged observed $[I > 2\sigma(I)]$. The structure was solved by direct methods (SHELXS-86)[12] and completed using difference Fourier synthesis (SHELXL-93).[13] All atoms, with the exception of the metal atoms, were refined with isotropic thermal parameters as a result of the paucity of data arising from the noncentrosymmetric nature of the space group and poor crystal quality. A total of 41 restraints were applied to idealize the geometry, but not the orientation, of the ReO_4^- anions, the NO_2Me solvent molecule, and some of the OMe carbon atoms. Final residual $wR_2 = 0.356$ for all data, correponding to a conventional *R* factor of 0.116 based on observed reflections.