10346 *J. Am. Chem. Soc.* **1994,** *116,* 10346-10347

Ball and Socket Nanostructures: New Supramolecular Chemistry Based on Cyclotriveratrylene

Jonathan W. Steed, Peter C. Junk, and Jerry L. Atwood*

Department of Chemistry, University of Missouri—Columbia
Columbia, Missouri 65211

Michael J. Barnes and Colin L. Raston*

Faculty of Science and Technology, Griffith University
Nathan, Brisbane 4111, Australia

Robert S. Burkhalter

Department of Chemistry, University of Alabama
Tuscaloosa, Alabama 35487

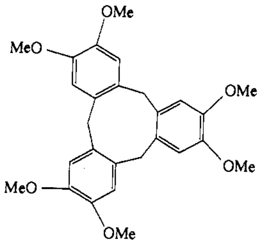
Received January 5, 1994
Revised Manuscript Received September 16, 1994

The readily available macrocycle cyclotriveratrylene (CTV, **1**) has been studied extensively in connection with its marked propensity to form inclusion compounds of the channel variety.[1] In these materials, guest molecules occupy voids in the crystalline lattice which result from the characteristic columnar stacking of the saucer-shaped CTV units.[2] Contemporary studies, however, have focused on related bowl-shaped host molecules such as the calixarenes, in which guest species are included within the cavity of the macrocycles, and it is clear that this type of supramolecular interaction offers much greater scope for guest selectivity and control of reactivity.[3]

Recently[4] we reported the use of calixarenes as a means toward the selective isolation of fullerenes C_{60} and C_{70} from fullerite (the crude mixture of fullerenes obtained by toluene extraction of carbon arc soot) and other mixtures. A cursory examination of the structure of CTV suggests that it, too, may exhibit fullerene inclusion properties, since these are likely to result from π–π charge transfer interactions, and it is possible that such complexes may be of the intrabowl type.

On standing at 20 °C for *ca.* 12 h, a 1:1 mixture of CTV and C_{60} in toluene yielded black crystalline plates of composition $(C_{60})_{1.5}(CTV)(toluene)_{0.5}$ (**2**), Scheme 1,[5] isolated in 10% yield. Increasing the amount of CTV to 10 equiv resulted in a 72% yield of the inclusion complex based on C_{60} with almost complete discharge of the purple color in the solution (the residual concentration of C_{60} was found to be around 10^{-4} M by UV–vis).[6] Under the same conditions, C_{70} did not form a complex, although fullerite gave a crystalline precipitate based exclusively upon C_{60} and C_{70} (established using FAB-MS, ^{13}C NMR and FT-IR spectroscopy, and HPLC[7]). The ratio C_{60}:C_{70} was variable, but the upper limit of C_{70} uptake was 72:28 for material from a single crystal.

Retrieval of the C_{60} and C_{70} from the CTV complexes is readily achieved by addition of chloroform or methylene chloride, whereupon the fullerenes precipitate as a black powder (>95% recovery). This decomposition of the inclusion complexes is probably related to the ability of halogenated hydrocarbon solvents to interact with the π-electron density of the host.[8]



1

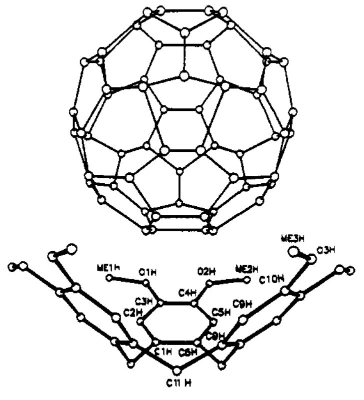


Figure 1. Molecular structure of the ball and socket $(C_{60})(CTV)$ structure found in $(C_{60})_{1.5}(CTV)(C_7H_8)_{0.5}$ (**2**). Intermolecular C_{60}–C_{CTV} contacts, 3.51 Å; C_{60}–O_{CTV}, 3.34 Å.

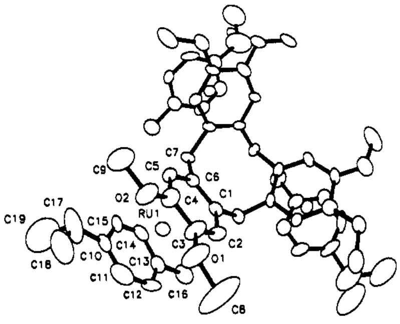
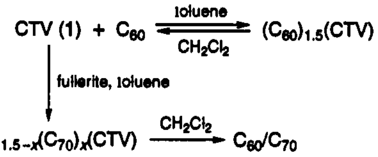


Figure 2. X-ray crystal structure of the molecular cation in $[\{Ru(\eta^6\text{-}MeC_6H_4\text{-}4\text{-}CHMe_2)\}_3(\eta^6{:}\eta^6{:}\eta^6\text{-}CTV)][BF_4]_6$ (**5**) showing the atom numbering scheme adopted.

Scheme 1



Crystals of $(C_{60})_{1.5}(CTV)(C_7H_8)_{0.5}$ (**2**) were grown *via* slow evaporation of a methylene chloride/toluene solution, and several X-ray diffraction data sets were collected from different crystals.[9] The structure confirms the stoichiometry established by analysis: the asymmetric unit comprises one half of a 1:1 $(C_{60})(CTV)$ complex (the other half generated by a mirror plane), one fourth of a highly disordered C_{60} residing over a $2/m$ site symmetry, and possibly a one fourth of a highly disordered toluene molecule of the same site symmetry. While the structure is of low precision as a consequence of this disorder, the $(C_{60})(CTV)$ complex gave a meaningful refinement, clearly showing docking of the fullerene with the CTV, Figure 1. The close contacts between the two

---

(1) (a) Collet, A. *Tetrahedron* **1987**, *43*, 5725. (b) Cagoliti, V.; Liquori, A. M.; Gallo, N.; Giglio, E.; Scrocco, M. *J. Inorg. Nucl. Chem.* **1958**, *8*, 572.

(2) (a) Steed, J. W.; Zhang, H.; Atwood, J. L. *Supramol. Chem.*, in press. (b) Zhang, H.; Atwood, J. L. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 465. (c) Cerrini, S.; Giglio, E.; Mazza, F.; Pavel, N. V. *Acta Crystallogr., Sect. B* **1979**, *35*, 2605. (d) Birnbaum, G. I.; Klug, D. D.; Ripmeester, J. A.; Tse, J. S. *Can. J. Chem.* **1985**, *63*, 3258.

(3) (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989. (b) Vincens, J.; Bohmer, V., Eds. *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.

(4) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229.

(5) C_{60} (30 mg, 0.042 mmol) was added to CTV (200 mg, 0.44 mmol) in toluene (30 mL), and the solution was refluxed for 5 min and then filtered. On the solution standing overnight, large black prisms formed, which were collected and washed with toluene. Yield: 35 mg (72%). Anal. Calcd for $C_{120.5}H_{34}O_6$: C, 91.74; H, 2.16. Found: C, 91.87; H, 2.06.

(6) Allemand, P.-M.; Koch, A.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(7) Meier, M. S.; Selegue, J. P. *J. Org. Chem.* **1992**, *57*, 1924.

(8) Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1994**, 15.

(9) Crystal data (298 K, Enraf-Nonius CAD4 diffractometer): $(C_{60})_{1.5}(CTV)(C_7H_8)_{0.5}$, $M_r = 1577.6$, monoclinic, $C2/m$, $a = 30.131(9)$, $b = 17.436(5)$, and $c = 14.638(5)$ Å, $\beta = 116.33(2)°$, $V = 6892$ Å^3, $Z = 4$, $D_c = 1.53$ g cm^{-3}, μ(Mo Kα) = 0.87 cm^{-1}, 5707 unique reflections with $2\theta_{max} = 50°$, 1813 with $I > 3\sigma(I)$ used in the refinement. The structure was solved by direct methods (SHELX-86) and refined using alternating full matrix least-squares and difference Fourier synthesis (SHELX-76). The well-defined $(C_{60})(CTV)$ complex resides across a mirror plane, whilst the highly disordered second fullerene and toluene of crystallization are located on a $2/m$ site. Final residuals: $R = 0.15$, $R' = 0.14$ (unit weights).

0002-7863/94/1516-10346$04.50/0

entities are at the van der Waals limits, C···C = 3.51 Å, C···O = 3.34 Å, the C···C contacts being reminiscent of the interaction between adjacent planes in graphite. The lack of disorder of this C_{60} relates to its contact with the rigid CTV molecule and also to the matching of symmetry elements; the 3-fold axis of the CTV coincides with a 3-fold axis of C_{60} such that the C-9 ring of CTV lines up with a C-6 ring of the fullerene, with the three immediate C-5 rings residing over the three aromatic rings of the CTV. The formation of a mixed C_{60}/C_{70} complex with CTV, but not of C_{70} with the same compound, can be rationalized by the crystallographic findings. The disordered C_{60} in the present structure seemingly acts as a space filler in the packing of the (C_{60})(CTV) units, in the ratio 1:2, and any C_{70} present may also act as a space filler in the same way.

The unprecedented inclusion of the C_{60} molecule within the bowl of the CTV host, in contrast to the usual stacking of one CTV unit within another,[2] prompted us to look at other ways in which the inclusion chemistry of CTV might be modified to incorporate this type of ball and socket motif. In the case of **2**, the unusual size and electronic requirements of the guest fullerene dominate the crystal packing. However, simple steric hindrance of the underside of the CTV bowl should prevent the close stacking of one CTV unit into another and thus result in ball and socket-type inclusion.

Recently, we showed that the binding of transition metal ions to the carbocyclic rings of the outer face of calixarenes can markedly modify the inclusion properties of the rings, resulting in the inclusion of polar and anionic guests within the macrocyclic cavity.[10] Similar metalation of CTV should result in the formation of new inclusion species in which the guest is held within the bowl of the CTV molecule, in close proximity to a redox active transition metal center, suggesting the basis for a class of molecular device which may function as a redox catalyst.

Pretreatment of $[\{Ru(\eta^6\text{-arene})Cl(\mu\text{-}Cl)\}_2]$ (**3**) (arene = $1\text{-}MeC_6H_4\text{-}4\text{-}CHMe_2$)[11] with $Ag[BF_4]$ followed by refluxing in CF_3CO_2H in the presence of a 0.5 molar equivalence of CTV resulted in the formation of the dicationic, mixed sandwich complex $[Ru(\eta^6\text{-arene})(\eta^6\text{-CTV})][BF_4]_2$ (**4**) in 95% yield. Similar treatment of **1** with excess **3** gave the 6+ species $[\{Ru(\eta^6\text{-arene})\}_3(\eta^6{:}\eta^6{:}\eta^6\text{-CTV})][BF_4]_6$ (**5**), again in excellent yield. The ^{1}H NMR spectra[12] of the new complexes showed unambiguously that, in the case of **4**, only one face of the CTV molecule is coordinated to the metal center. Complex **5** exhibits a single set of signals markedly shifted from the free ligand values. Notably, both **4** and **5** exhibit *two* residual H_2O signals in the $NO_2Me\text{-}d_3$ solvent in each case (δ 2.32 and 2.13 for **4**; δ 2.62 and 2.10 for **5**) which may correspond to intra- and extracavity water. In the solid state, the Nujol mull infrared spectrum of **4** exhibits a strong, broad band at 3480 cm^{-1}, suggesting the presence of enclathrated water.

The formulations of **4** and **5** were confirmed by FAB mass spectrometry. In the case of **4**, a strong molecular ion peak was observed as well as a signal corresponding to the molecular cation in association with one tetrafluoroborate anion. For **5**, strong peaks were observed for the molecular cation in association with five, four, and three tetrafluoroborate anions. The formulation of **5** was also verified by a single crystal X-ray structure determination,[13] Figure 2.

Surprisingly for such a complex salt, **5** belongs to the cubic space group $Pa\bar{3}$, with $a = 25.173(2)$ Å. Like the parent CTV molecule and related structures, the cation adopts the expected bowl-shaped crown conformation, but, in this case, the macrocycle is situated upon a 3-fold rotation axis. The absence of 3-fold rotational symmetry in previous structures of CTV and related compounds has been taken to be evidence for the absence of homoaromaticity[2] throughout the CTV molecule as a whole, with one ring being generally pushed away from the other two. In the present structure, it is possible that the reduced π-electron density on each ring is sufficient to reduce these intramolecular inter-annular repulsions, as is often seen for metal complexes of [2.2]-paracyclophane.[14] As in the parent CTV molecule, the cation adopts a shallow bowl conformation with the intercentroid separation d = 4.52 Å, compared to 4.70–4.96 Å in the free ligand.[2] The Ru–C_{CTV} distances fall into two distinct groups with longer bonds to the upper-rim carbon atoms C(3) and C(4), 2.31(2) Å (av) compared to 2.20(2) Å (av) for the remaining atoms, possibly as a consequence of unfavorable steric interactions between the isopropyl group of the *p*-cymene ligand and the methoxy substituents of the CTV rings. Within the asymmetric unit, one of the two tetrafluoroborate anions is disordered over three sites: two of these sites are situated upon 3-fold rotation axes, while, most importantly, the final anion is distributed in a highly disordered fashion within the cavity of the CTV host. This disorder probably arises from a size mismatch between that small BF_4^- anion and the large, shallow cavity of the CTV. This contrasts to the BF_4^- inclusion species $[\{Ru(p\text{-cymene})\}_4(\text{calix}[4]\text{arene}-2H)][BF_4]_6$ recently reported by us, in which the anion is well defined and penetrates deeply within the calixarene cavity.[10] The structure does, however, demonstrate the principles that (i) the characteristic packing of free CTV may be disrupted such as to allow guest molecules to enter the cavity and (ii) the electronic properties of the electron-rich CTV cavity may be modified by appending of transition metal centers in order to allow the inclusion of anionic guest species.

In conclusion, this paper outlines new vistas for the inclusion chemistry of hosts based upon the cyclotriveratrylene motif. A simple method of retrieving pure fullerenes from fullerite without the use of chromatographic techniques has been outlined, and a new class of ball and socket-type inclusion species has been realized by simple modification of either host or guest electronic and steric properties.

Acknowledgment. We are grateful to the National Science Foundation, the Australian Research Council, and the Department of Industry, Technology and Regional Development (Australia) for support of this work and to SERC/NATO for the award of a research fellowship (to J.W.S.).

Supplementary Material Available: Tables giving crystal data and details of the structure determination, atomic coordinates, thermal parameters, and bond lengths and angles for **2** and **5** (16 pages); listing of observed and calculated structure factors for **2** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(10) Steed, J. W.; Juneja, R. K.; Atwood, J. L. *Angew. Chem.*, in press.

(11) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(12) ^{1}H NMR data ($NO_2Me\text{-}d_3$, 200 MHz, 20 °C, δ/ppm, J/Hz): for **4**, δ 7.33 (s, 2H, coordinated CTV ring), 7.15 (s, 4H, uncoordinated CTV rings), 6.99, 6.90 (AB, 4H, ^3J = 6.6, *p*-cymene ring), 4.75, 3.80 (AB, 4H, ^2J = 13.7, proximal CH_2), 4.63, 3.79 (AB, 2H, ^2J = 14.1, distal CH_2), 4.22 (s, 6H, OMe), 3.88 (s, 6H, OMe), 3.86 (s, 6H, OMe), 2.95 (sp, 1H, ^3J = 6.7, C*H*Me$_2$), 2.61 (s, 3H, Me), 1.41 (d, 6H, ^3J = 6.7, CH*Me*$_2$); for **5**, δ 7.37 (s, 6H, CTV ring), 6.98 (s, 12H, *p*-cymene ring), 4.56, 3.85 (AB, 6H, ^2J = 10.2, CH_2), 4.24 (s, 18H, OMe), 3.04 (sp, 3H, ^3J = 6.7, C*H*Me$_2$), 2.73 (s, 9H, Me), 1.50 (d, 18H, ^3J = 6.7, CH*Me*$_2$); for **5**, δ 7.72 (s, 4H, Ir-coordinated CTV rings), 7.41 (s, 2H, Ru-coordinated CTV ring), 7.02 (s, 4H, *p*-cymene ring), 4.58 (m, 3H, CH_2), 3.88 (m, 3H, CH_2), 4.28 (s, 18H, OMe), 3.04 (sp, 1H, ^3J = 6.5, C*H*Me$_2$), 2.65 (s, 3H, Me), 2.40 (s, 30H, Cp*), 1.41 (d, 6H, ^3J = 6.5, CH*Me*$_2$).

(13) Crystal data: $C_{57}H_{72}O_6Ru_3\cdot 6BF_4\cdot 9H_2O$, M_r = 1839.36, yellow plate, cubic, $Pa\bar{3}$, a = 25.173(2) Å, V = 15 953(3) Å^3, Z = 8, D_c = 1.54 g cm^{-3}, μ(Mo Kα) = 6.61 cm^{-1}. Of 5357 data collected on an Enraf-Nonius CAD4 diffractometer (2θ = 4–50° at 20 °C), 3400 were independent and 1775 were judged observed [$I > 3\sigma(I)$]. Data were corrected for Lorentz, polarization, and absorption effects (ψ-scans) and for crystal decay (34%). The structure was solved and refined as for **2**. The asymmetric unit was found to contain one third of one cationic molecule and a total of two tetrafluoroborate anions. The final difference electron density map also revealed the presence of three significant peaks corresponding to disordered solvent of crystallization, probably water. The remaining tetrafluoroborate anion was found to be disordered over three sites and, as a consequence, was extremely poorly defined. The final refinement converged with R = 0.079, R' = 0.083 (unit weights).

(14) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (b) Elsegood, M. R. J.; Tocher, D. A. *J. Organomet. Chem.* **1990**, *391*, 239.