

Molecule II, $[\text{MoAs}_2\text{Se}_{10}]^{2-}$, obtained by the same procedure as I, but isolated as the *n*-butyl ammonium salt, contains one molybdenum atom chelated by two AsSe_3 groups (see Figure 2).¹³ Again, the metal is apical and there are two selenium atoms in the base instead of arsenic atoms. The coordinated selenium atoms of the two cages are rotated 24° away from fully eclipsing each other. In addition, one of the corners of each cage is tipped toward the other. This tipping is quite pronounced and does not appear to be caused by any steric crowding or crystal-packing effects. All of the other distances and angles in the molecule appear to be reasonable and are nearly identical with those in I.¹⁴ Gouy measurements show that this molecule is also diamagnetic.

The close $\text{Se}(2)\cdots\text{Se}(2a)$ contact is 2.702 (4) Å. This is somewhat long for a true Se-Se bond, which is usually on the order of 2.35 Å. However, the distance is considerably shorter than a van der Waals interaction and has been assigned as bonding in other selenium cage molecules.¹⁵ Alternatively, it may also be caused by a somewhat crowded coordination environment created by the large selenium atoms around a high-valent molybdenum. The distances between the other corner selenium atoms (3.017 (4) Å) can be considered beyond bonding distance. The short Se-Se interaction in II leads to some difficulty in assigning formal oxidation states. If the Se-Se interaction is not considered, there is a formal charge of 4+ on the metal site. However, a bond between the two selenium atoms results in a formal oxidation state of 2+ on the molybdenum. The unusual environment around the bonded selenides does not lead to any substantial differences in the bond lengths to the metal center (2.500 (3) Å versus 2.47 (4) Å).

The reason for the unusual tipping is not clear at this point. To our knowledge there is no precedent for this type of behavior. There have been several examples of hybrid transition-metal-main-group cages reported in the literature, but most could be explained by using classical bonding arguments.⁵

Both I and II are isolated in low yields, but the procedure is simple enough that reasonable amounts of each product can be obtained conveniently. Use of other arsenic selenide sources leads to similar products but no improvement in yield. The molecules are thermally stable if protected from air and are soluble in polar aprotic solvents, but all attempts to recrystallize them do not lead to any cleaner products. Nevertheless, we have demonstrated a reasonable synthetic entry to a novel series of mixed main-group transition-metal cages.

Acknowledgment. We are indebted to the National Science Foundation for support of this work (CHE-8802217).

Registry No. $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{W}_2\text{As}_2\text{Se}_{13}]$, 130984-14-4; $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{W}_2\text{As}_2\text{Se}_{13}]\cdot(\text{CH}_3)_2\text{NCOH}$, 130984-15-5; $[(n\text{-Bu})_4\text{N}]_2[\text{MoAs}_2\text{Se}_{10}]$, 130955-19-0; $[\text{Ph}_4\text{P}]_2[\text{WSe}_4]$, 112988-67-7; $[(n\text{-Nu})_4\text{N}]_2[\text{MoSe}_4]$, 130955-20-3; As_4Se_4 , 12006-05-2.

Supplementary Material Available: Complete structural data, listing of positional and thermal parameters for all atoms, complete distances and angles, and hydrogen atom coordinates for molecules I and II (12 pages); listing of observed and calculated structure factors for molecules I and II (33 pages). Ordering information is given on any current masthead page.

(13) Crystal structure data for $[(\text{C}_6\text{H}_5)_4\text{N}]_2[\text{MoAs}_2\text{Se}_{10}]$: deep purple parallelepiped sealed in epoxy, space group monoclinic, $C2/c$, $a = 18.277$ (9) Å, $b = 15.445$ (8) Å, $c = 17.983$ (7) Å, $\beta = 104.04$ (4)°, $V = 4925$ (4) Å³, $Z = 4$, $D_{\text{calcd}} = 2.05$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 89.31$ cm⁻¹, ψ scans (transmission factors 0.74-1.00), $T = 21$ °C. Measured 3348 reflections ($3.5^\circ \leq 2\theta \leq 45^\circ$), of which 3227 were unique ($R_{\text{int}} = 0.072$); data were corrected for absorption by using the ψ scan technique; refinement used 1898 reflections with $F_o^2 > 2.58\sigma(F_o^2)$ and resulted in residuals of $R = 0.0667$ and $R_w = 0.0752$ (214 parameters; all non-hydrogen atoms anisotropic).

(14) It is difficult to distinguish between arsenic and selenium atoms on the basis of crystallography alone, and it could be postulated that these atoms might be trivalent arsenic. However, this would conflict with elemental analysis and would still provide an electron counting problem, since this distance is too long to be a legitimate As-As single bond.

(15) (a) McMullan, R. K.; Prince, D. J.; Corbett, J. D. *Inorg. Chem.* 1971, 10, 1749. (b) Gillespie, R. J. *Chem. Soc. Rev.* 1979, 8, 315.

Self-Assembly of a Hydrogen-Bonded 2 + 3 Supramolecular Complex¹

Christopher T. Seto and George M. Whitesides*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received August 13, 1990

We are designing and synthesizing three-dimensional supramolecular assemblies based on the pattern of hydrogen bonds present in the 1:1 complex between cyanuric acid and melamine (CA·M). We have previously shown that hubM_3 (Scheme I) organizes three melamine units into a geometry compatible with the CA·M lattice and forms a 1:3 complex with neohexyl cyanurate.² Here we report that hubM_3 reacts with the bis(cyanuric acid) $\text{R}(\text{CA})_2$ (Scheme I) in CHCl_3 and forms a 2:3 complex, $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$, that incorporates two layers of the CA·M lattice into a well-defined three-dimensional structure.^{3,4}

We monitored the titration of hubM_3 in CDCl_3 with aliquots of $\text{R}(\text{CA})_2$ by ¹H NMR spectroscopy (Figure 1). The spectrum of uncomplexed hubM_3 (bottom trace) has resonances that are broadened by self-association and restricted rotation around the amide and RNH-triazine bonds. At intermediate points in the titration, the spectrum shows resonances for $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$ against a background of uncomplexed hubM_3 . The complex appears to be predominantly a single conformation, and exchange between $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$ and uncomplexed hubM_3 in solution is slow on the NMR time scale. Beyond the 2:3 stoichiometry, there is no further change in the spectrum. The hubM_3 units in $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$ are chiral. From the ¹H NMR spectrum, we cannot tell whether the complex exists as a racemic mixture of *R,R* and *S,S* species or as a meso compound, *R,S*. The simplicity of the spectrum suggests, however, that only racemic or meso complexes are present, and not a mixture of the two.

Two features of Figure 1 support the assigned structure for $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$: First, several equivalent protons of hubM_3 (g, g'; q, q'; and r, r') and $\text{R}(\text{CA})_2$ (w, w' and x, x') are diastereotopic in $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$ and thus appear as separate resonances. Second, the two sets of imide NH protons (y, y') of $\text{R}(\text{CA})_2$ are in different hydrogen-bonding environments and thus appear as separate resonances in the complex, even though they are equivalent by symmetry in uncomplexed $\text{R}(\text{CA})_2$. NOE studies also support our proposed structure. We observed several positive intermolecular NOEs between hubM_3 and $\text{R}(\text{CA})_2$ that are consistent with a CPK model of the $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$ complex (Scheme I). The NOEs between the imide NH protons (y, y') of $\text{R}(\text{CA})_2$ and the melamine NH protons (n, o, o', p) of hubM_3 confirm the 3-fold nature of the hydrogen-bonded network.

Two other analytical methods support the 2:3 stoichiometry of $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$. Vapor pressure osmometry (VPO) of the complex indicated $\text{MW} \approx 5300$ (calcd for $(\text{hubM}_3)_2(\text{R}(\text{CA})_2)_3$: 5519) over the concentration range 2-16 mM in CHCl_3 at 37 °C with a sucrose octaacetate standard.⁵ Titration of hubM_3 (0.1 mM in CH_2Cl_2) with $\text{R}(\text{CA})_2$ monitored by UV spectroscopy also indicated a 2:3 complex.⁶

(1) The National Science Foundation supported this work (Grants CHE-88-12709 to G.M.W. and DMR-89-20490 to the Harvard University Materials Research Laboratory).

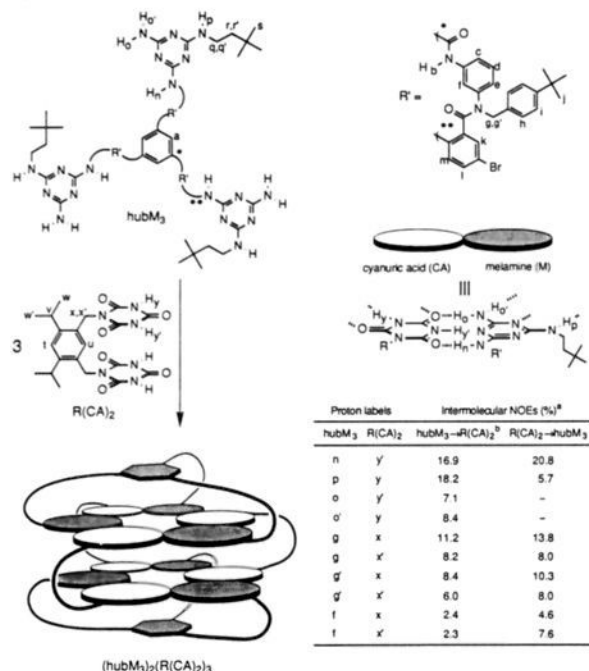
(2) Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* 1990, 112, 6409-6411.

(3) For other supramolecular assemblies, see: Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 245-255 and references therein. Bryant, J.; Ericson, J.; Cram, D. J. *Am. Chem. Soc.* 1990, 112, 1255-1256. Etter, M. *Acc. Chem. Res.* 1990, 23, 120-126. Manka, J. S.; Lawrence, D. S. *J. Am. Chem. Soc.* 1990, 112, 2440-2442. Ashton, P.; Goodnow, T.; Kaifer, A.; Reddington, M.; Slawin, A.; Spencer, N.; Stoddart, J.; Vincent, C.; Williams, D. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1396-1399.

(4) All new compounds gave satisfactory ¹H NMR (500 MHz), ¹³C NMR (125 MHz), and elemental analyses.

(5) The molecular weight of the complex estimated by using other standards was as follows ($\text{MW}_{\text{complex}}$, standard $\text{MW}_{\text{standard}}$): 5890, perbenzoyl β -cyclodextrin 3321; 5390, polystyrene 5050 (polydispersity = 1.05); 4430, *N,N'*-bis(*tert*-butyloxycarbonyl)gramicidin S 1342. We suggest that the gramicidin S derivative was associated in solution and, hence, unsuitable as a standard.

Scheme I. Self-Assembly of hubM₃ with R(CA)₂ To Give a Supramolecular 2:3 Complex



^a Intermolecular NOEs between hubM₃ and R(CA)₂ in the 2:3 complex are given in the table. The complex (10 mM) in CDCl₃ was degassed with five freeze-pump-thaw cycles, and the NOE difference spectra were taken at 500 MHz with a presaturation time of 3.0 s. ^b hubM₃→R(CA)₂ represents irradiation of the proton on hubM₃ and observation of an NOE at the proton of R(CA)₂.

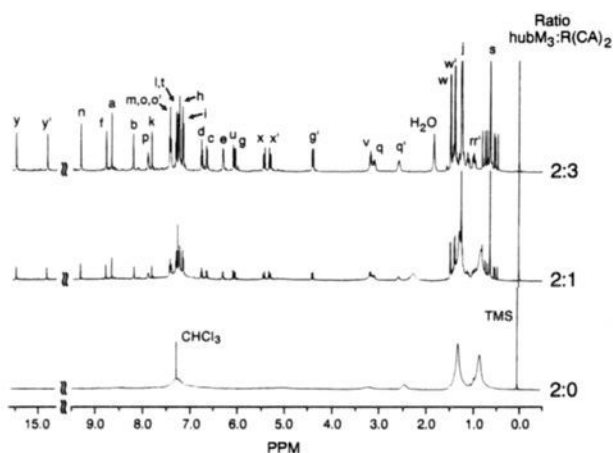


Figure 1. ¹H NMR titration of hubM₃ (500 MHz, 10 mM in CDCl₃) with R(CA)₂. The peak assignments are shown at the top of the figure. We believe that the small peaks in the base line of the upper spectrum correspond to conformational isomers of the 2:3 complex. These minor peaks are not impurities in either of the individual components. R(CA)₂ alone is too insoluble to give a detectable spectrum at saturation (<0.1 mM) in CDCl₃ at the instrument gain used here.

Formation of the (hubM₃)₂(R(CA)₂)₃ complex is an unfavorable process entropically: five particles combine into a single particle; the spokes of hubM₃ are constrained to one conformation. The complex is stable only because the enthalpy gained by forming the 36 hydrogen bonds in the complex is large enough to compensate for the entropic factor.

This procedure points the way to the synthesis of large molecular assemblies by a process based on self-assembly of stable hydrogen-bonding networks, rather than formation of covalent bonds.

(6) UV data: uncomplexed hubM₃ λ_{max} = 269 nm (ε = 94 050 M⁻¹ cm⁻¹); (hubM₃)₂(R(CA)₂)₃ λ_{max} = 255 nm (ε = 100 200 M⁻¹ cm⁻¹).

In that sense, its strategy is more closely modeled on the principles that determine secondary and tertiary structure in proteins and nucleic acids than on the methods used in classical organic synthesis. Future papers will describe the synthesis of structures more complex than (hubM₃)₂(R(CA)₂)₃.

Acknowledgment. NMR instrumentation was supported by National Science Foundation Grant CHE-84-10774. We thank Professor Robert Cohen (MIT, Chemical Engineering) for the loan of the vapor pressure osmometer.

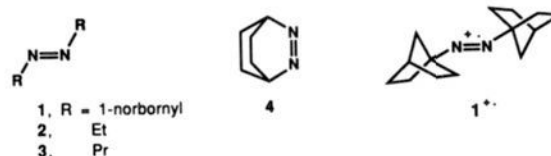
1,1'-Azonorbornane Radical Cation. A Solution-Stable Azoalkane Radical Cation

Maria E. Mendicino and Silas C. Blackstock*

Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235

Received October 5, 1990

The discovery by Engel, Shine, and co-workers¹ of fast deazetative fragmentation of 1,1'-azoadamantane upon one-electron oxidation has sparked general interest in the nature of azoalkane radical cations, their fragmentation mechanism, and their usefulness as precursors to various radical, cation, and radical cation systems.¹⁻⁶ Azoalkane radical cations are short-lived species and, to date, have been observed only under matrix-isolation conditions by low-temperature ESR spectroscopy. Some azoalkane radical cations are even too reactive to survive matrix isolation.⁴ Here we present the first example of a solution-stable azo radical cation system and report preliminary physical data for this species.



Electrochemical oxidation of 1,1'-azonorbornane⁷ (1) by cyclic voltammetry⁸ (CV) yields a chemically reversible voltammogram ($E^{\circ'} = 1.40$ V vs SCE, $E_{pp} = 60$ mV), indicating a solution lifetime for 1⁺ of at least seconds. Chemical oxidation of 1 in cold CH₂Cl₂ by 1 molar equiv of tris(2,4-dibromophenyl)-ammonium hexachloroantimonate, Ar₃N⁺SbCl₆⁻, results in decolorization of the green oxidant upon mixing. The resulting yellow solution shows a five-line ESR signal assigned as a(2N)

(1) Bae, D. H.; Engel, P. S.; Hoque, A. K. M. M.; Keys, D. E.; Lee, W.-K.; Shaw, R. W.; Shine, H. J. *J. Am. Chem. Soc.* **1985**, *107*, 2561.

(2) (a) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964. (b) Shine, H. J.; Bae, D. H.; Hoque, A. K. M. M.; Kajstura, A.; Lee, W. K.; Shaw, R. W.; Soroka, M. *Phosphorus Sulfur* **1985**, *23*, 111. (c) Engel, P. S.; Kitamura, A.; Keys, D. E. *J. Org. Chem.* **1987**, *52*, 5015.

(3) (a) Adam, W.; Casado, A.; Miranda, M. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 797. (b) Adam, W.; Dorr, M. *J. Am. Chem. Soc.* **1987**, *109*, 1570. (c) Adam, W.; Grabowski, S.; Miranda, M. A.; Rubenacker, M. *J. Chem. Soc., Chem. Commun.* **1988**, 142.

(4) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484.

(5) (a) Rhodes, C. J.; Louwries, P. W. F. *J. Chem. Res., Synop.* **1988**, 38. (b) Rhodes, C. J. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 3215. (c) Rhodes, C. J. *J. Chem. Soc., Chem. Commun.* **1990**, 799.

(6) (a) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887. (b) Gerson, F.; Qin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498.

(7) (a) Golzke, V.; Groeger, F.; Oberlinner, A.; Ruchardt, C. *Nouv. J. Chim.* **1978**, *2*, 169. (b) Schmittl, M.; Ruchardt, C. *J. Am. Chem. Soc.* **1987**, *109*, 2750. (c) Neuman, R. C., Jr.; Grow, R. H.; Binegar, G. A.; Gunderson, H. J. *J. Org. Chem.* **1990**, *55*, 2682. 1 has been prepared in 63% overall yield from 1-aminonorbornane by *m*-CPBA oxidation to 1-nitrosonorbornane followed by Si₂Cl₆ reduction of the nitroso dimer.

(8) Electrochemistry is performed at a planar Pt disk working electrode in 0.1 M TBAP/acetonitrile at room temperature at scan rates of 20-2000 mV s⁻¹.