Acetonitrile solutions of (mesitylene)Mo(CO)3, 1.5 equiv. Et4NCN, and 0.25 equiv. M+ afford the inorganic tetrahedranes (Et4N)5[Mo(CO)3(μ-CN)6(CO)12] (M = Na, Li), the strained nature of which is indicated by their ready reaction with CsO3SCF3 to give trigonal prismatic (Et4N)8[Cs(μ-CN)3]4−.

We have reported that the cyanometallate box [Cp*Rh2][Mo(CO)3]2(μ-CN)2− selectively binds Cs+ (vs. K+).1 This mirrors behavior exhibited by solid state cyanometallates, which have been of interest for radiowaste separations.2,3 We have recently discovered that in cyanometallate cages with labile M–CN bonds, Cs+ and K+ promote the formation of trigonal prismatic, not cubic, cages, e.g. [Cs2Mo(CO)3(μ-CN)3]4−.4 We now report that use of the smaller Na+ (rD¼ 116 pm) and Li+ (rD¼ 90 pm) ions in place of Cs+ (rD¼ 181 pm) and K+ (rD¼ 152 pm) in the Mo–CO/CN− system affords tetrahedral cages, a third member of the series [M⊂[Mo(μ-CN)3]6L4]−.1 This result establishes that the alkali metal not only templates cage formation, but that the size of the alkalai metal ion determines the cage structure. Of further interest, tetrahedral M⊂[Mo(μ-CN)6] cages are unprecedented within the area of cyanometallates.5

Treatment of acetonitrile solutions of (mesitylene)Mo(CO)3 with 1.5 equiv. Et4NCN in the presence of 0.25 equiv. NaSbF6 gives a yellow solution from which golden crystals, analyzed as (Et4N)5[NaMo(CO)3(μ-CN)6(CO)12], can be precipitated in 77% yield.6,† 159 MHz 23Na NMR spectroscopy indicates that this reaction is complete within 1 h. The IR spectrum shows that the anion is rather electron rich (Δυ(CO)¼ 1997, 1876, 1745 cm−1). X-Ray diffraction analysis revealed an anionic tetrahedrane with four Mo(CO)3 vertices and six μ-CN edges (Fig. 1). Not unlike [K2Mo6(μ-CN)9(CO)18]−, each Mo atom is octahedral with acute CN–Mo–CN angles (81.2°) and 90° C–Mo–CO angles. The Na+–CN distance of ca. 2.56 Å is comparable to that in Na-alkyls.6–10 The Mo–CN linkages are bent with Mo–CN–N/C angles (82.1°) and 90° C–Mo–CO angles. The Na+–C/N interatomic distance (ca. 185 pm) is smaller than the Na–C distance in Na-alkyls.6–10

The availability of two classes of cages of formula M⊂[Mo(μ-CN)3]4(μ-CN)2(μ3–C)4 (M = Cs, K, n = 6 vs. M = Na, Li, n = 4) prompted a study of their interconversion. Cage interconversion is also relevant to cage assembly mechanisms, a topic that has only recently come under scrutiny.12 The 233 MHz 7Li NMR spectrum of Li⊂[Mo(CO)3]2 in MeCN consists of a single signal at δ¼ 0.28 (apparently the Na chemical shift is insensitive to the CN linkage isomerism). On addition of one equiv. of LiO3SCF3 to a MeCN solution of square (Et4N)4-Mo⊂[Mo(μ-CN)3]4(μ3–C)4 as small amounts of Li⊂[Mo(μ-CN)3]6L4(μ3–C)4 becomes dominant. Further Et4NCN, however, degrades the Li⊂[Mo(CO)3]3 region and breakdown of Li⊂[Mo(CO)3]3− becomes dominant. Further Et4NCN, however, degrades the Li⊂[Mo(CO)3]3− giving only Mo⊂[Mo(CO)3]3− and free Li+.4 Similar observations were obtained by 23Na NMR spectroscopy for the formation of Na⊂[Mo(CO)3]3– from NaSbF6 and I. These results confirm the ready formation of the tetrahedrane when Mo⊂[Mo(CO)3]3−, CN−, and the alkali metal are present in the appropriate ratio.
The literature on tetrahedral cages is rapidly growing, although the previously reported cages are guided by the directionality and denticity of organic ligands, whereas in the present case only CN\(^{-}\) is the linker and guidance is provided by the size of the encapsulated ion.

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Notes and references

1. Synthesis of (Et\(_4\)N\(_4\))[Na\(_2\)Mo\(_5\)O\(_{12}\)(μ-CN)\(_3\)(CO\(_3\))\(_2\)] (1). A solution of 156 mg (1.00 mmol) Et\(_4\)NC in 15 mL MeCN was added dropwise to a stirred solution of 200 mg (0.666 mmol) (mesitylene)Mo(CO)\(_3\) and 43 mg (0.167 mmol) NaSbF\(_6\) in 10 mL MeCN. The resulting solution was allowed to stand for 18 h and then 100 mL Et\(_2\)O was added to precipitate the product as a yellow powder. The product was collected by filtration, washed twice with 10 mL portions of Et\(_2\)O, and dried under vacuum for 12 h. Yield 210 mg (77%). IR (υ\(_{\text{CN}}\), KBr/cm\(^{-1}\)): 2089 (w), 1997 (vs), 1934 (m), 1876 (vs), 1745 (vs). Anal. Calc. (found) for Cs\(_2\)H\(_{100}\)Mo\(_4\)Na\(_{11}\)O\(_{12}\): C, 44.94 (45.02); H, 6.50 (6.62); Mo, 24.75 (24.53); Na, 1.48 (1.42); N, 9.94 (10.10%).

3. Complementarily, 79 MHz \(^{133}\)Cs NMR measurements vs. [Li(MeCN)\(_4\)]\(^+\) showed that excess alkali metal does not degrade the cage. Using substoichiometric amounts of NaSbF\(_6\) showed only formation of Na\(_2\)CT\(^{5-}\). Thus, alkali metal is required for cage formation, only the tetrahedral cage forms at low stoichiometry, and excess alkali metal does not affect cage formation.

Notes and references