Alkali metal-templated assembly of the tetrahedral cyanometallate cages $[\mathrm{M{\subset}Mo_4(\mu\text{-}CN)_6(CO)_{12}}]^{5-}$ (M = Li, Na)

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Received (in Irvine, CA, USA) 11th December 2000, Accepted 16th January 2001

Acetonitrile solutions of (mesitylene)Mo(CO)$_3$, 1.5 equiv. Et$_4$NCN, and 0.25 equiv M$^+$ afford the inorganic tetrahedranes (Et$_4$N)$_5$[M⊂Mo$_4$(μ-CN)$_6$(CO)$_{12}$] (M = Na, Li), the strained nature of which is indicated by their ready reaction with CsO$_3$SCF$_3$ to give trigonal prismatic (Et$_4$N)$_8$[Cs⊂Mo$_6$(μ-CN)$_9$(CO)$_{18}$].

We have reported that the cyanometallate box [Cp*Rh]$_4$[Mo(CO)$_3$]$_4$(μ-CN)$_{12}$$^{4-}$ 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.* [Cs⊂Mo$_6$(μ-CN)$_9$(CO)$_{18}$].[4] We now report that use of the smaller Na$^+$ (r_{ionic} = 116 pm[5]) and Li$^+$ (r_{ionic} = 90 pm) ions in place of Cs$^+$ (r_{ionic} = 181 pm) and K$^+$ (r_{ionic} = 152 pm) in the Mo–CO/CN$^-$ system affords tetrahedral cages, a third member of the series $\{\mathrm{M{\subset}[Mo(\mu\text{-}CN)_{1.5}L_x]_n}\}^{(1.5n-1)-}$. This result establishes that the alkali metal not only templates cage formation, but that *the size of the alkali metal ion determines the cage structure*. Of further interest, tetrahedral M$_4$(μ-CN)$_6$ cages are unprecedented within the area of cyanometallates.[2]

Treatment of acetonitrile solutions of (mesitylene)Mo(CO)$_3$ with 1.5 equiv. Et$_4$NCN in the presence of 0.25 equiv. NaSbF$_6$ gives a yellow solution from which golden crystals, analyzed as (Et$_4$N)$_5$[Na⊂Mo$_4$(μ-CN)$_6$(CO)$_{12}$] (Na⊂T^{5-}), can be precipitated in 77% yield.†‡ 159 MHz ^{23}Na NMR spectroscopy indicates that this reaction is complete within 1 h. The IR spectrum shows that the anion is rather electron rich (ν_{CO} = 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 [K⊂Mo$_6$(μ-CN)$_9$(CO)$_{18}$]$^{8-}$ (K⊂TP^{8-}),[4] each Mo atom is octahedral with acute CN–Mo–CN angles (82.1°) and 90° C–Mo–CO angles. The Na$^+$–C/N distance of *ca.* 2.56 Å is comparable to that in Na-alkyls.[6–10] The Mo–CN linkages are bent with Mo–C/N–N/C bond angles of 165.9°. In the molecular triangle Re$_3$(μ−CN)$_3$(CO)$_{12}$, the M–C–N angles are *ca.* 180° with most of the bending occurring at the *ca.* 135° M–N–C angles.[11] A similar situation may apply to Na⊂T^{5-} but the presence of four structurally similar linkage isomers, each of which can adopt four different orientations in the crystal structure, made this difficult to establish unambiguously. Evidence for the four different possible linkage isomers comes from ^{13}C NMR spectroscopy (Fig. 2), which shows the predicted 16 signals in the μ-CN region. The Li$^+$-containing tetrahedrane, (Et$_4$N)$_5$[Li⊂Mo$_4$(μ-CN)$_6$(CO)$_{12}$] (Li⊂T^{5-}), was prepared from (mesitylene)Mo(CO)$_3$, 1.5 equiv. Et$_4$NCN, and 0.25 equiv. LiO$_3$SCF$_3$.

The availability of two classes of cages of formula $\mathrm{M{\subset}[Mo(\mu\text{-}CN)_{1.5}(CO)_3]_n}^{(1.5n-1)-}$ (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 ^{7}Li NMR spectrum of Li⊂T^{5-} in MeCN consists of a single signal at δ −0.28 (apparently the Na chemical shift is insensitive to the CN linkage isomerism). On addition of one equiv. of LiO$_3$SCF$_3$ to a MeCN solution of square (Et$_4$N)$_4$-[Cs⊂Mo$_6$(μ-CN)$_9$(CO)$_{18}$] (**1**),[4] a broad signal at δ −1.8 as well as small amounts of Li⊂T^{5-} (Fig. 3) were observed. Upon adjusting the CN$^-$: Mo(CO)$_3$ ratio to 1.5, the signal for Li⊂T^{5-} becomes dominant. Further Et$_4$NCN, however, degrades the Li⊂T^{5-} giving only Mo(CO)$_3$(CN)$_3$$^{3-}$ and free Li$^+$.[4] Similar observations were obtained by ^{23}Na NMR spectroscopy for the formation of Na⊂T^{5-} from NaSbF$_6$ and **1**. These results confirm the ready formation of the tetrahedrane when Mo(CO)$_3$, CN$^-$, and the alkali metal are present in the appropriate ratio.

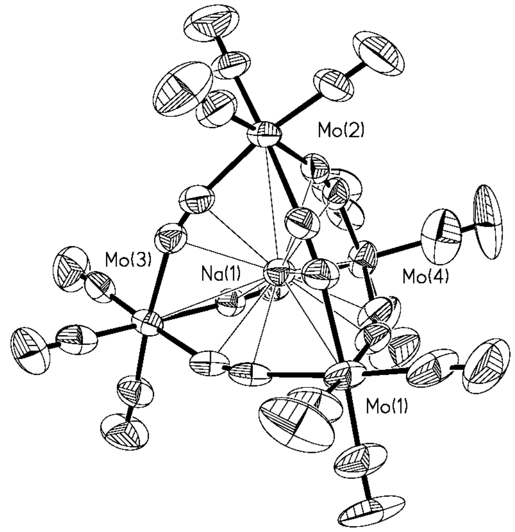


Fig. 1 Structure of the anion in (Et$_4$N)$_5$[Na⊂Mo(μ-CN)$_6$(CO)$_{12}$]·4MeCN with thermal ellipsoids set at the 50% probability level. Selected average distances (Å) and angles (°): Mo–C/N 2.25, Mo–CO 1.93, Na–C/N 2.56, C/N–Mo–C/N 82.1, OC–Mo–CO 90.0; Mo–C/N–Mo 165.9.

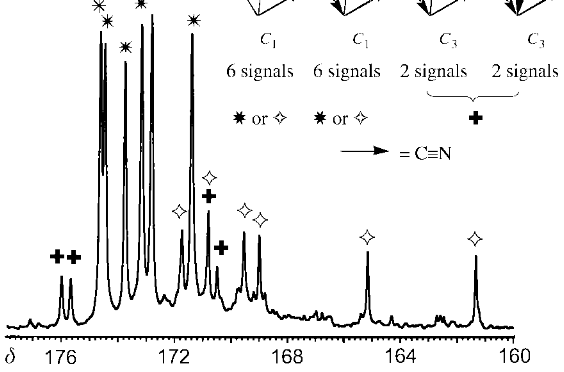


Fig. 2 187.5 MHz ^{13}C NMR spectrum of (Et$_4$N)$_5$[Na⊂Mo(μ-CN)$_6$(CO)$_{12}$] showing the 14 signals observed in the μ-CN region and breakdown of signals into groups attributable to the four linkage isomers.

DOI: 10.1039/b010192n

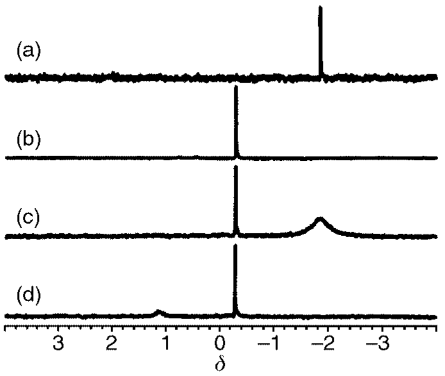
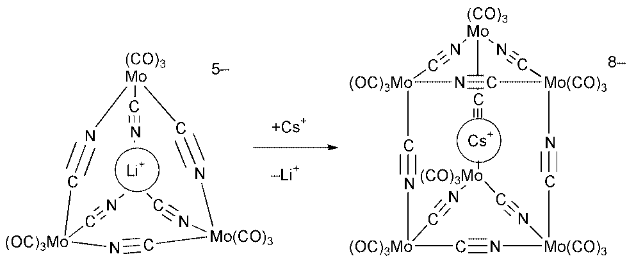


Fig. 3 233.2 MHz ^{7}Li NMR spectra illustrating the effect of Mo : CN ratio on cage synthesis (MeCN solutions): (a) 0.18 M LiO_3SCF_3; (b) 0.018 M $(Et_4N)_5[Li{\subset}Mo(\mu\text{-}CN)_6(CO)_{12}]$; (c) 0.019 M $(Et_4N)_4\{[Mo(CO)_3(NCMe)]_4(CN)_4\}$ and 0.019 M LiO_3SCF_3; and (d) 0.019 M $(Et_4N)_4\{[Mo(CO)_3(NCMe)]_4(CN)_4\}$, 0.019 M LiO_3SCF_3 and 0.038 M Et_4NCN.

We also examined the effect of alkali metal stoichiometry. Addition of one equiv. $NaSbF_6$ to a solution of $Na{\subset}T^{5-}$ gave a broad ^{23}Na NMR signal for Na^+ centered at δ −4.5 along with undiminished signal for $Na{\subset}T^{5-}$, indicating that excess alkali metal does not degrade the cage. Using substoichiometric amounts of $NaSbF_6$ shows only formation of $Na{\subset}T^{5-}$. 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.

Experiments involving mixed alkali metals clarified the relative thermodynamic and kinetic stabilities of the new families of CN-based cages. LiO_3SCF_3 has no effect on the ^{23}Na spectrum of $Na{\subset}T^{5-}$ whereas one equiv of $NaSbF_6$ converts $Li{\subset}T^{5-}$ into $Na{\subset}T^{5-}$. This reaction is likely due to the better fit of the sodium ion within the cavity and may also be partially driven by the entropic advantage for encapsulation of $[Na(MeCN)_6]^+$ *vs.* $[Li(MeCN)_4]^+$.[13,14] ^{7}Li NMR measurements showed that one equiv. of CsO_3SCF_3 causes release of free Li^+ from $Li{\subset}T^{5-}$. Complementarily, 79 MHz ^{133}Cs NMR measurements showed that Cs^+ converts both $Na{\subset}T^{5-}$ and $Li{\subset}T^{5-}$ predominantly into $Cs{\subset}TP^{8-}$ (Scheme 1). Consistent with the greater stability of the larger cages, the ^{133}Cs NMR spectrum of $Cs{\subset}TP^{8-}$ is unaffected by the presence of Li^+, Na^+, and K^+. The higher reactivity of the tetrahedral cages is attributed to the weakened M-NC bonding associated with strained Mo–C–N–Mo angles (*vide supra*).



$[Li{\subset}Mo_4(\mu\text{-}CN)_6(CO)_{12}]^{5-}$ $[Cs{\subset}Mo_6(\mu\text{-}CN)_9(CO)_{18}]^{8-}$

Scheme 1

The literature on tetrahedral cages is rapidly growing,[15–18] 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.

This research was supported by the Department of Energy. We thank Dr Paul Molitor for assistance with the NMR measurements.

Notes and references

† *Synthesis* of $(Et_4N)_5[Na{\subset}Mo_4(\mu\text{-}CN)_6(CO)_{12}]$ (**1**). A solution of 156 mg (1.00 mmol) Et_4NCN 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_2O was added to precipitate the product as a yellow powder. The product was collected by filtration, washed twice with 10 mL portions of Et_2O, and dried under vacuum for 12 h. Yield 210 mg (77%). IR ($\nu_{C\equiv X}$, KBr/cm^{-1}): 2089 (w), 1997 (vw), 1934 (m), 1876 (vs), 1745 (vs). Anal. Calc. (found) for $C_{58}H_{100}Mo_4NaN_{11}O_{12}$: 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)%. The Li derivative was prepared identically using LiOTf in place of $NaSbF_6$. Single crystals of **1** were grown from MeCN solutions by vapor diffusion using ether.

‡ *Crystal data* for **1**: M = 1550.3, monoclinic, space group $P2_1/c$, a = 19.1292(16), b = 19.3643(16), c = 24.966(2) Å, β = 96.764°, Z = 4, D_c = 1.290 Mg m^{-3}, λ = 0.71073 Å, μ = 0.601 mm^{-1}, $R1$ = 0.0735, $wR2$ = 0.1894, GoF = 1.0098.

CCDC 13795. See http://www.rsc.org/suppdata/cc/b0/b010192n/ for crystallographic data in .cif or other electronic format.

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