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[18] The FerroTANE ligands and rhodium catalysts are available for both research and commercial use through Chirotech Technology Ltd.

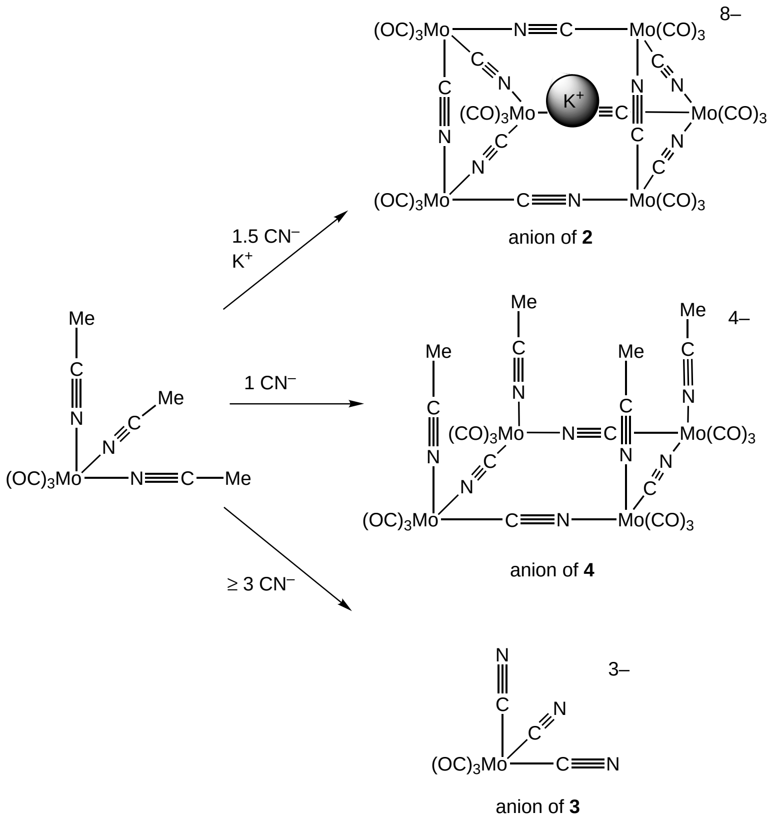
$\{K \subset [Mo_6(\mu\text{-}CN)_9(CO)_{18}]\}^{8-}$: A Trigonal-Prismatic Cyanometalate Cage[**]

Stephen M. Contakes and
Thomas B. Rauchfuss[*]

Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

The preeminent cyanometalate is Prussian Blue. Prussian Blue and its many analogues feature cubic or incomplete cubic arrays of metals linked by μ-CN units.[1, 2] The Prussian Blue motif is the basis of a new generation of high T_c magnets,[3, 4] molecular bowls and boxes[5, 6] with novel ion-binding properties,[7] and unusual coordination polymers.[8] Isoelectronic analogies between [$L_nFe^{II}CN$] and [L_nMo^0CN] suggest that it should be possible to prepare families of cages based on Prussian Blue employing cyano derivatives of the Group 6 metal–carbonyl complexes [$M(CO)_6$].[9] Relevant to this plan is the well-recognized ability of cyanide to accomodate high negative charge, for example [$Ni(CN)_4$]$^{4-}$.[10, 11]

We have examined the reaction of (Et_4N)CN in MeCN with [Mo(Mes)(CO)$_3$] (**1**, Mes = mesitylene = 1,3,5-$Me_3C_6H_3$), the latter serving as a convenient source of [Mo(CO)$_3$-(MeCN)$_3$].[7] When solutions of **1** and (Et_4N)CN in MeCN are combined in a 6:9 ratio in the presence of KPF_6, one obtains $(Et_4N)_8\{K \subset [Mo_6(\mu\text{-}CN)_9(CO)_{18}]\}$ (**2**) as yellow microcrystals in quantitative yield (Scheme 1). Crystallographic analysis reveals that **2** consists of a trigonal-prismatic $Mo_6(CN)_9$ cage with idealized D_{3h} symmetry (Figure 1). Eight Et_4N^+ ions are evident in the asymmetric unit. At the center of the cage lies a potassium cation. The potassium is formally 18-coordinate, but the K⋯C/N bonding is ionic. The potassium atom is 3.37 and 3.20 Å from the C/N atoms of the triangular and square faces, respectively. The Mo centers are octahedral with all OC-Mo-CO angles of about 84° and C/N-Mo-CO of about 96°. The average C/N-Mo-C/N angle within the square faces is 85°, and within the triangular faces it is 80°. The ring strain associated with the 60° Mo⋯Mo⋯Mo angles is also responsible for the acute Mo-C-N/Mo-N-C angles of 169° observed for the triangluar faces (versus 178° for the square faces). Because of disorder between the C and N sites, the Mo–C/N distance of 2.23 Å represents an average of Mo–N(C) and Mo–C(N) distances. In similar compounds, the $(CO)_3Mo^0$–[μ-NC]$_3$ distance is about 2.2 Å.[7] This implies that Mo–CN and Mo–NC distances are similar, especially in view of the small thermal parameters for C/N atoms. The Cs^+ analogue of **2** was also crystallographically characterized,



Scheme 1. Synthesis of **2**–**4**.

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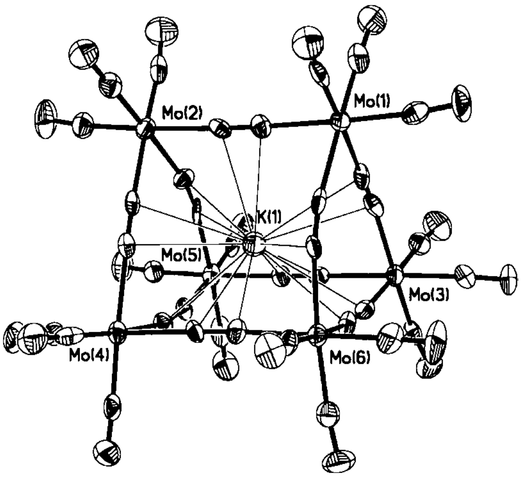
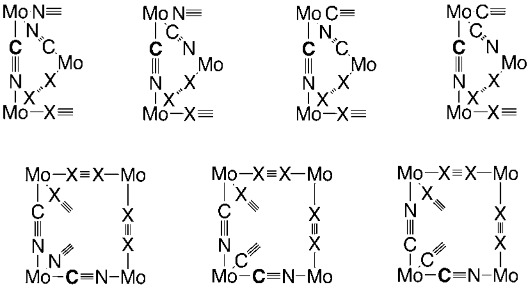


Figure 1. Structure of the anion in **2**, with thermal ellipsoids drawn at the 50 % probability level. Selected average bond lengths [Å] and angles [°]: Mo-CN/NC (triangle) 2.24, Mo-CN/NC (square) 2.23, Mo-CO 1.95, C-N 1.17, C-O 1.19, K-C/N (triangle) 3.37, K-C/N (square) 3.20, Mo⋯Mo (within triangular faces) 5.56, Mo⋯Mo (between triangular faces) 5.63; C/N-Mo-C/N (triangle) 80, C/N-Mo-C/N (square) 85, Mo-C-N/Mo-N-C (triangle) 169, Mo-C-N/Mo-N-C (square) 178, OC-Mo-CO 84, OC-Mo-CN 96.

although the refinement suffered from disorder involving the Et_4N^+ ions.

The ^{13}C NMR measurements on the Cs^+ analogue of **2**, prepared from a single crystal that was ^{13}C-enriched (33 %) at CN^-, revealed a series of seven broad peaks at $\delta = 169.0$, 170.0, 170.0, 171.5, 172.0, 173.0, and 174.0 in the μ-CN region.[12] The occurrence of several CN signals reflects the structural complexity of **2**, which exists as a mixture of isostructural linkage isomers. In fact, when only the local environment about each Mo center in **2** is considered, there are seven different CN coordination sites (Scheme 2).



Scheme 2. Coordination sites for CN units in **2**. The relevant C atom is always shown in boldface.

While solutions of **1** react rapidly with $(Et_4N)CN$ at all stoichiometries—the reaction with more than 3 equiv provides $(Et_4N)_3[Mo(CO)_3(CN)_3]$ (**3**, Scheme 1)—we obtained a spectroscopically pure material only for the 1:1 reaction (in the absence of alkali metal templating ions!). This 1:1 product is the square $(Et_4N)_4[Mo_4(\mu\text{-}CN)_4(CO)_{12}(MeCN)_4]$ (**4**). In **4**, the four MeCN ligands are disposed on the same side of the ring, which is unusual (Figure 2). The packing diagram shows that the squares pack as dimers, such that one NCMe group of one square inserts into the $(MeCN)_4Mo_4(CN)_4$ "nest" of a partner square (Figure 3). We propose the "all-up" isomer is stabilized by this nesting interaction. With its preorganized square subunit, **4** is a probable precursor to **2**. The four MeCN ligands in **4** are tilted towards the interior of the square, which will favor the formation of triangular faces; other M-CN triangles are known.[13–15]

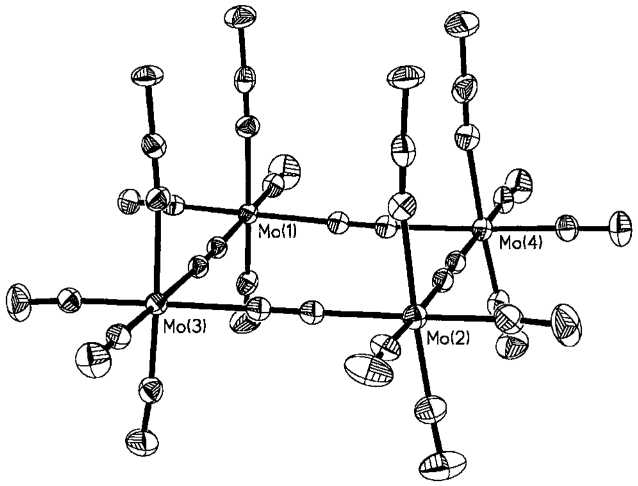


Figure 2. Structure of the anion in **4**, with thermal ellipsoids drawn at the 50 % probability level. Selected average bond lengths [Å] and angles [°]: Mo-C/N 2.24, Mo-CO 1.94, Mo-NCMe 2.26, C-N 1.15, C-O 1.17, Mo⋯Mo 5.62; C/N-Mo-C/N 86, C/N-Mo-NCMe 85, Mo-C-N 177, Mo-N-CMe 176.

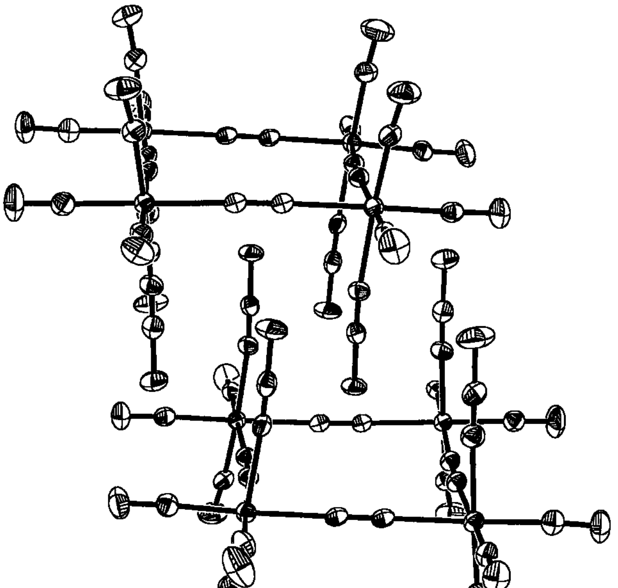


Figure 3. Packing of two anions in **4**, with thermal ellipsoids drawn at the 50 % probability level. The distance between the two parallel $Mo_4(\mu\text{-}CN)_4$ planes is 7.10 Å, and the Mo-NC-Me distance is 4.86 Å.

In summary, this work establishes a new cage geometry, the trigonal prism, and a novel coordination environment for potassium. More generally, these results demonstrate that classical metal–carbonyl complexes are promising precursors to cyanometalate cages.

Experimental Section

2: A solution of KPF_6 (13 mg, 0.071 mmol), $(Et_4N)CN$ (100 mg, 0.641 mmol), and **1** (128 mg, 0.427 mmol)[16] in MeCN (10 mL) was stirred at room temperature for 1 h. The solvent was reduced to about 5 mL, and Et_2O (15 mL) was added to precipitate yellow microcrystals; yield: 149 mg (88 %). IR (KBr): $\tilde{\nu}_{C\equiv X} = 2094, 2085, 1998, 1934, 1881, 1756\ cm^{-1}$; elemental analysis calcd for $C_{91}H_{160}KMo_6N_{17}O_{18}$ (found): C 45.63 (44.14), H 6.73 (7.21), N 9.94 (10.33), Mo 24.03 (23.63), K 1.63 (1.45). The low carbon microanalysis is attributed to the formation of refractory KMo_6C phases, as indicated by elemental analysis and thermogravimetric analysis (TGA). The Cs^+ analogue of **2** was prepared similarly. Crystals of **2** were grown from $MeCN/Et_2O$.

3: A suspension of **1** (100 mg, 0.333 mmol) and $(Et_4N)CN$ (156 mg, 1.00 mmol) in MeCN (20 mL) was heated at reflux for 3 h. The solvent was reduced to about 5 mL, and Et_2O (30 mL) was added to precipitate the colorless product, which was washed with Et_2O; yield: 196 mg (91 %). IR (KBr): $\tilde{\nu}_{C\equiv X} = 2093, 2067, 1935, 1879, 1763\ cm^{-1}$; IR (MeCN): $\tilde{\nu}_{C\equiv X} = 2086, 1884, 1870, 1760\ cm^{-1}$; IR ($CD_2Cl_2$): $\tilde{\nu}_{C\equiv X} = 2076, 2066, 1867, 1740\ cm^{-1}$; ^{13}C NMR (^{13}C-labeled (33 %) sample, 100 MHz, CD_2Cl_2): $\delta = 163.45$ (s); elemental analysis calcd for $C_{30}H_{60}MoN_6O_3$ (found): C 51.27 (50.92), H 9.47 (9.20), N 11.96 (12.23), Mo 14.79 (15.00). The K^+ salt of $[Mo(CO)_3(CN)_3]^{3-}$ has been previously described by Hieber et al.[17]

4: A solution of $(Et_4N)CN$ (52 mg, 0.333 mmol) and **1** (100 mg, 0.333 mol) in MeCN (15 mL) was stirred for 4 h. Filtration followed by addition of Et_2O (25 mL) to the golden solution gave a white powder, which was washed with Et_2O; yield: 90 mg (72 %). IR (MeCN): $\tilde{\nu}_{C\equiv X} = 2290, 2100, 1902, 1888, 1772\ cm^{-1}$; elemental analysis calcd for $C_{56}H_{94}Mo_4N_{12}O$ (found): C 44.04 (44.12), H 6.20 (6.07), N 11.01 (11.05).

Crystals of **2** and **4**, mounted on glass fibers using Paratone-N (Exxon), were analyzed on a Siemens Platform/CCD automated diffractometer at 198 K. The data were processed with SHELXTL. The structures were solved using direct methods and refined using full-matrix least squares on F^2 with the program SHELXL-93. Hydrogen atoms were fixed in idealized positions with thermal parameters 1.5 × those of the attached carbon atoms. Data were corrected for absorption on the basis of Ψ scans.

Crystal data for **2** ($C_{99}H_{162}N_{21}O_{18}Mo_6K$): $M_r = 2543.19$, monoclinic, space group $P2_1/c$, $a = 14.8474(9)$, $b = 28.8113(18)$, $c = 27.6760(17)$ Å, $\beta = 91.157(2)^\circ$, $V = 11836.6(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.427\ Mg\,m^{-3}$, $F(000) = 5268$, 1408 parameters; $R_1 = 0.0664$, $R_w = 0.1277$, GOF = 0.881 for all 20849 data ($I > 2\sigma(I)$); max./min. residual electron density 1.050/−0.680 e$^-$ Å^{-3}.

Crystal data for **4** ($C_{68}H_{110}N_{18}O_{12}Mo_4$): $M_r = 1755.50$, triclinic, space group $P\bar{1}$, $a = 16.0533(6)$, $b = 16.3657(7)$, $c = 19.9581(8)$ Å, $\alpha = 67.8040(10)$, $\beta = 68.2200(10)$, $\gamma = 67.7400(10)^\circ$, $V = 4331.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.346\ Mg\,m^{-3}$, $F(000) = 1816$, 991 parameters; $R_1 = 0.0415$, $R_w = 0.0929$, GOF = 0.841 for all 19722 data ($I > 2\sigma(I)$); max./min. residual electron density 0.706/−0.433 e$^-$ Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133912 (**2**), -137914 (the Cs^+ analogue of **2**), -133859 (**3**), and -137913 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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