Supporting Information for

[Mo₁₆O₅₃F₂]¹²⁻; A new polyoxofluoromolybdate anion

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Table S1. Bond Valence Sums^a for [C₆H₁₃N₂]₂[C₆H₁₄N₂][Mo₈O₂₆].

S_i	Mo1	Mo2	Mo3	Mo4	Mo5	Mo6	Mo7	Mo8	ΣS_i
O1	1.69								1.69
O2	1.71								1.71
O3	0.91	0.97							1.88
O4	1.01		0.97						1.98
O5	0.38				1.45				1.83
O6	0.20	0.35	0.32	0.57	0.30				1.74
O7		1.72							1.72
O8		1.72							1.72
O9		0.77		0.89		0.32			1.98
O10		0.28			0.85	0.8			1.93
O11			1.74						1.74
O12			1.71						1.71
O13			0.33		0.92		0.76		2.01
O14			0.76	0.86			0.31		1.93
O15				1.81					1.81
O16				1.45				0.39	1.84
O17				0.31	0.58	0.28	0.30	0.27	1.74
O18					1.76				1.76
O19						1.76			1.76
O20						1.71			1.71
O21						1.02		0.95	1.97
O22							1.71		1.71
O23							1.72		1.72
O24							1.01	0.87	1.88
O25								1.68	1.68
O26								1.75	1.75
ΣS_i	5.90	5.81	5.83	5.89	5.86	5.89	5.81	5.91	

^a Valence sums calculated with the formula $S_i = \exp[(R_0 - R_i)/B]$, where S_i is the bond valence of bond 'i,' R_0 is a constant dependent upon the bonded elements, R_i is the bond length of bond 'i,' and B equals 0.37. ΣS_i is the bond valence sum for each atom. R_0 (Mo^{VI}–O) = 1.907.

Table S2. Bond Valence Sums for [C₆H₁₄N₂]₆[Mo₁₆O₅₃F₂]₄·4H₂O.^b

<i>S_i</i>	Mo1	Mo2	Mo3	Mo4	Mo5	Mo6	Mo7	Mo8	Σ <i>S_i</i>
F1	0.70								0.70
O1	1.67								1.67
O2	1.72								1.72
O3	0.44	0.34	1.06						1.84
O4	0.55		0.50		0.95				2.00
O5	0.88	0.83							1.71
O6		1.64							1.64
O7		1.75							1.75
O8		0.93		0.90					1.83
O9		0.38	0.24	0.44		0.89			1.95
O10			1.71						1.71
O11			0.91		0.42	0.25	0.47		2.05
O12			1.56	0.29					1.85
O13				1.66					1.66
O14				1.69					1.69
O15				1.00		0.50		0.47	1.97
O16					1.63				1.63
O17					1.55				1.55
O18					0.27	1.52			1.79
O19					1.09		0.77		1.86
O20						1.71			1.71
O21						1.06	0.35	0.40	1.81
O22							1.70		1.70
O23							1.04	0.67	1.71
O24							1.64		1.64
O25								1.73	1.73
O26								1.64	1.64
O27								1.00	2.00
Σ <i>S_i</i>	5.96	5.87	5.98	5.98	5.91	5.93	5.97	5.91	

^b R₀ (Mo^{VI}–F) = 1.81.

Table S3. Bond Valence Sums for γ -[Mo₈O₂₆]⁴⁻.^{c,d}

S_i	Mo1	Mo2	Mo3	Mo4	ΣS_i
O1	1.78				1.78
O2	1.07		0.30	0.51	1.88
O3	1.00	0.44		0.20	1.85
	0.20				
O4	1.54	0.29			1.83
O5		1.73			1.73
O6		1.02		0.94	1.96
O7		1.77			1.77
O8	0.35	0.75	1.04		2.14
O9			1.75		1.75
O10			1.75		1.75
O11			1.23	0.79	2.03
O12				1.72	1.72
O13				1.81	1.81
ΣS_i	5.95	5.99	6.06	5.98	

^c $R_0(\text{Mo}^{\text{VI}}-\text{F}) = 1.81$. ^d Bond lengths for the γ -[Mo₈O₂₆]⁴⁻ anion were taken from Niven, M. L.; Cruywagen, J. J.; Heyns, J. B. B. *J. Chem. Soc. Dalton Trans.* **1991**, 2007.

Figure S1. Three-dimensional packing of **1**. Red octahedra, white circles and blue circles represent MoO₆, carbon atoms and nitrogen atoms, respectively. Hydrogen atoms have been removed for clarity.

Description of the hydrogen-bonding in **1**.

$[\text{C}_6\text{H}_{13}\text{N}_2]_2[\text{C}_6\text{H}_{14}\text{N}_2][\text{Mo}_8\text{O}_{26}]$ (**1**) contains three complete DABCO molecules in the asymmetric unit. Two of these molecules are singly protonated, exhibiting the formula $[\text{C}_6\text{H}_{13}\text{N}_2]^+$, while the third is doubly protonated as $[\text{C}_6\text{H}_{14}\text{N}_2]^{2+}$. The partial protonation DABCO molecules is required for reasons of charge balance. **1** contains well known β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ molecular anions, necessitating a total charge of 4+ on three DABCO molecules. Hydrogen placement was based upon two factors, H site location from difference maps and hydrogen bonding interactions. Four of the six nitrogen sites, N1, N2, N4 and N5, on the three DABCO molecules exhibit N – O non-contact distances that are consistent with hydrogen bonds, ranging between 2.826(9) – 2.985(9) Å. The remaining two nitrogen sites, N3 and N6, do not show interatomic distances that correspond to hydrogen bonds. In fact, N3 and N6 are oriented towards other DABCO molecules instead of oxide hydrogen bond acceptors. The location of hydrogen bond sites from difference maps corresponds directly to those identified through inspection of possible hydrogen-bonding interactions.