Facile Synthesis of Mononuclear Early Transition-Metal Complexes of κ^3 *cyclo*-tetraphosphate ($[P_4O_{12}]^{4-}$) and *cyclo*-triphosphate ($[P_3O_9]^{3-}$)†

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1 X-ray Crystallographic Details

Yellow crystals of $[TBA]_3[(P_4O_{12})Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ and $[PPN]_2[(P_3O_9)VOF_2]\cdot 2CH_2Cl_2$ and colorless crystals of $[TBA]_3[(P_4O_{12})MoO_2Cl]$ were grown from a mixture of diethyl ether and dichloromethane. Yellow crystals of $[PPN]_2[(P_3O_9)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$ were grown from vapor diffusion of diethyl ether into a diluted dichloromethane solution. Colorless crystals of $[PPN]_2[(P_3O_9)MoO_2Cl]$ and $[PPN]_2[(P_3O_9)WO_2Cl]$ were grown from vapor diffusion of diethyl ether into a saturated acetonitrile. Green crystals crystals of $[PPN]_2[(P_3O_9)MoOCl_2]$ were grown from a mixture of dichloromethane:toluene (2:1).

Low-temperature (100 K) data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, ϕ- and ω-scans). General refinement details have been described elsewhere.[1,2] All structures exhibited disorders, and generally, to all of the disordered atoms similarity restraints were applied on 1–2

and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters; the ratio between the components of each disorder was refined freely and constrained to unity. Specific details are provided in the text and tables below, and in the form of *.cif* files available from the CCDC.[3]

Complex **3** crystallized in the orthorhombic space group $P2_12_12_1$ with one anion, three cations, and one dichloromethane solvent molecule per asymmetric unit, with the allyl and two carbonyl ligands disordered together over two positions (52:48). Complex **5** crystallized in the monoclinic space group $P2_1/c$ with one anion, three cations, and one dichloromethane solvent molecule per asymmetric unit; in addition to parts of five butyl arms and the solvent molecule being disordered, the cation also exhibits a minor disorder component (85:15) stemming from the chloride ligand on the metal being disordered over two positions. Complex **7** crystallized in the monoclinic space group with *Cc* with one anion and two cations per asymmetric unit, and no solvent or any disorders present, but the crystal was merohedrally twinned. Complex **8** crystallized in the monoclinic space group $P2_1/c$ with one anion, two cations, and no solvent in the asymmetric unit; only a minor disorder was present stemming from the distribution of the chloride metal ligand over two positions (95:5). Complex **9** crystallized in the triclinic space group $P\bar{1}$ with half of anion and one anion per asymmetric unit, and the anion was disordered over two unrelated positions (68:32) and refined to a half total occupancy. Complex **10** crystallized in the triclinic space group $P\bar{1}$ with one anion, two cations, and two dichloromethane solvent molecules, one of which was disordered over two positions. Complex **11** crystalized in the monoclinic space group $P2_1/c$ with one anion and two cations per asymmetric unit, with a minor disordered component stemming from the distribution of the chloride metal ligand over two positions (95:5).

2 IR Tables

Table S1 Selected IR stretches for salts **2**, **3**, **4**, and **5** (cm^{-1})

Salt	$\nu_{C\equiv O}$	ν_{M-O}
2	1874 (s)	
	1702 (s)	
	1708 (s)	
3	1898 (s)	
	1709 (s)	
4		896 (m)
		880 (m)
5		912 (m)

2:$[TBA]_4[(P_4O_{12})Mo(CO)_3]\cdot 2H_2O$; **3**:$[TBA]_3[(P_4O_{12})Mo(CO)_2(\eta^3\text{-}C_3H_5)]$; **4**:$[TBA]_3[(P_4O_{12})MoO_2Cl]$; **5**:$[TBA]_3[(P_4O_{12})VOF_2]\cdot Et_2O$.

Table S2 Selected IR stretches for complexes **6**, **7**, **8**, **9**, **10**, and **11** (cm^{-1})

Complex	$\nu_{C\equiv O}$	ν_{M-O}
6	1883 (s)	
	1723 (s)	
7	1812 (s)	
	1928 (s)	
8		923 (m)
		898 (m)
9		932 (m)
10		930 (m)
11		938 (m)
		907 (m)

6:$[PPN]_3[(P_3O_9)Mo(CO)_3]$; **7**:$[PPN]_2[(P_3O_9)Mo(CO)_2(\eta^3\text{-}C_3H_5)]$; **8**:$[PPN]_2[(P_3O_9)MoO_2Cl]$; **9**:$[PPN]_2[(P_3O_9)MoOCl_2]$; **10**:$[PPN]_2[(P_3O_9)VOF_2]\cdot 2CH_2Cl_2$; **11**:$[PPN]_2[(P_3O_9)WO_2Cl]$.

3 Crystallographic tables

Table S3 Geometry of hydrogen bonds and short intramolecular contacts

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	∠ D−H···A (°)
C1s−H1s2···O41[a]	0.99	2.048	3.065	170
C1s−H1s1···O33[b]	0.99	2.289	3.253	164
C1s−H1s1···F2[c]	0.99	2.494	3.377	148

[a] $[TBA]_3[(P_4O_{12})Mo(CO)_2(\eta^3\text{-}C_3H_5)]$; [b] $[TBA]_3[(P_4O_{12})MoO_2Cl]$; [c] $[PPN]_2[(P_3O_9)VOF_2]\cdot 2CH_2Cl_2$.

Table S4 Crystallographic data of complexes **2** and **4**

	[TBA]$_3$[(P$_4$O$_{12}$)Mo(CO)$_2$(η^3-C$_3$H$_5$)] (**2**)	[TBA]$_3$[(P$_4$O$_{12}$)MoO$_2$Cl] (**4**)
Identification code/CCDC	12008/898621	12053/928308
Empirical formula	$C_{216}H_{460}Cl_8Mo_4N_{12}O_{56}P_{16}$	$C_{49}H_{110}Cl_3Mo_1N_3O_{14}P_4$
Formula weight (g/mol)	5284.84	1291.57
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions	a = 12.1845(16) Å α= 90°.	a = 12.722(2) Å α= 90°.
	b = 23.687(3) Å β= 90°.	b = 23.246(4) Å β= 99.933(3)°.
	c = 23.769(3) Å γ= 90°.	c = 23.461(4) Å γ= 90°.
Volume	6860.1(15) Å^3	6834(2) Å^3
Z	1	4
Density (calculated)	1.279 Mg/m^3	1.255 Mg/m^3
Absorption coefficient	0.420 mm^{-}1	0.458 mm^{-1}
F(000)	2832	2760
Crystal size	0.40 x 0.22 x 0.05 mm^3	0.30 x 0.30 x 0.05 mm^3
Theta range for data collection	1.88 to 25.03°.	1.24 to 30.51°.
Index ranges	$-14 \leq h \leq 14$,	$-18 \leq h \leq 18$,
	$-28 \leq k \leq 28$,	$-33 \leq k \leq 33$,
	$-27 \leq l \leq 28$	$-33 \leq l \leq 33$
Reflections collected	113188	160859
Independent reflections	12130 [R$_{int}$ = 0.0607]	20812 [R$_{int}$ = 0.0476]
Completeness to theta max. (%)	28.55° 100.0%	30.51° 99.8%
Max. and min. transmission	0.9793 and 0.8500	0.9775 and 0.8749
Data / restraints / parameters	16919 / 2 / 883	20812 / 1129 / 966
Goodness-of-fit on F^2	1.044	1.048
Final R indices [I>2σ(I)]	R$_1$ = 0.0617, ωR$_2$ = 0.1425	R$_1$ = 0.0668, ωR$_2$ = 0.1730
R indices (all data)	R$_1$ = 0.0232, ωR$_2$ = 0.0600	R$_1$ = 0.0921, ωR$_2$ = 0.1939
Largest diff. peak and hole	1.248 and −1.273 e.Å^{-3}	–1.199 and −0.643 e.Å^{-3}

Table S5 Crystallographic data of complexes **7** and **8**

	[PPN]$_2$[(P$_3$O$_9$)Mo(CO)$_2$(η^3-C$_3$H$_5$)] (**7**)	[PPN]$_2$[(P$_3$O$_9$)MoO$_2$Cl] (**8**)
Identification code/CCDC	11209/928307	12036/898619
Empirical formula	$C_{77}H_{65}Mo_1N_2O_{11}P_7$	$C_{72}H_{60}Cl_1Mo_1N_2O_{11}P_7$
Formula weight (g/mol)	1507.04	1477.40
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$
Unit cell dimensions	a = 29.874(5) Å α= 90°.	a = 23.790(3) Å α= 90°.
	b = 13.005(2)Å β= 122.553(2)°.	b = 13.7091(15) Å β= 112.902(2)°.
	c = 20.899(3) Å γ = 90°.	c = 22.003(2) Å γ = 90°.
Volume	6844.2(19) Å^3	6610.1(12) Å^3
Z	4	4
Density (calculated)	1.463 Mg/m^3	1.485 Mg/m^3
Absorption coefficient	0.420 mm^{-1}	0.473 mm^{-1}
F(000)	3104	3032
Crystal size	0.75 x 0.24 x 0.14 mm^3	0.50 x 0.10 x 0.10 mm^3
Theta range for data collection	1.62 to 28.55°.	1.75 to 29.57°.
Index ranges	$-40 \leq h \leq 39$,	$-33 \leq h \leq 33$,
	$-17 \leq k \leq 17$,	$-19 \leq k \leq 19$,
	$-28 \leq l \leq 28$	$-30 \leq l \leq 30$
Reflections collected	69452	174550
Independent reflections	16919 [R_{int} = 0.0258]	18472 [R_{int} = 0.0742]
Completeness to theta max. (%)	28.55°. 99.7%	29.57°. 99.8%
Max. and min. transmission	0.9435 and 0.7434	0.9543 and 0.7980
Data / restraints / parameters	12130 / 234 / 810	18472 / 27 / 884
Goodness-of-fit on F^2	1.027	1.025
Final R indices [I>2σ(I)]	R_1 = 0.0225, ωR_2 = 0.0593	R_1 = 0.0349, ωR_2 = 0.0738
R indices (all data)	R_1 = 0.0726, ωR_2 = 0.1503	R_1 = 0.0534, ωR_2 = 0.0831
Largest diff. peak and hole	0.327 and −0.304 e.Å^{-3}	0.519 and −0.526 e.Å^{-3}

Table S6 Crystallographic data of complexes **9**, **10** and **11**

	$[PPN]_2[(P_3O_9)MoOCl_2]$ (**9**)	$[PPN]_2[(P_3O_9)VOF_2]\cdot 2CH_2Cl_2$ (**10**)	$[PPN]_2[(P_3O_9)WO_2Cl]$ (**11**)
Identification code/CCDC	12083/898620	12063/898623	12086/898624
Empirical formula	$C_{72}H_{60}Cl_2\ Mo_1N_2O_{10}P_7$	$C_{74}H_{64}Cl_4F_2N_2O_{10}P_7V_1$	$C_{72}H_{60}Cl_1N_2O_{11}P_7W_1$
Formula weight (g/mol)	1496.85	1588.80	1565.31
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a = 10.8738(14) Å α= 63.331(2)°.	a = 10.7925 (12) Å α = 83.503 (2)°.	a = 23.8075(18) Å α= 90°.
	b = 12.8662(16) Å β= 87.802(2)°.	b = 13.5617 (14) Å β = 84.906 (2)°.	b = 13.7219(11) Å β= 113.0000(10)°.
	c = 13.5974(17) Å γ = 80.090(2)°.	c = 24.724 (3) Å γ = 88.089 (2)°.	c = 22.0782(17) Å γ = 90°.
Volume	1673.0(4) Å^3	3580.2 (7) Å^3	6639.2(9) Å^3
Z	1	2	4
Density (calculated)	1.486 Mg/m^3	1.474 Mg/m^3	1.566 Mg/m^3
Absorption coefficient	0.505 mm^{-1}	0.51 $^{-1}$	2.013 mm^{-1}
F(000)	767	1632	3160
Crystal size	0.26 x 0.23 x 0.09 mm^3	0.35 x 0.25 x 0.08 mm^3	0.40 x 0.35 x 0.25 mm^3
Theta range for data collection	1.80 to 30.51°.	1.6 to 30.5°.	1.75 to 30.51°.
Index ranges	$-15 \leq h \leq 15$,	$-15 \leq h \leq 15$,	$-34 \leq h \leq 33$,
	$-18 \leq k \leq 18$,	$-19 \leq k \leq 19$,	$-19 \leq k \leq 19$,
	$-19 \leq l \leq 19$	$-35 \leq l \leq 35$	$-31 \leq l \leq 31$
Reflections collected	46986	21764	184026
Independent reflections	10155 [R_{int} = 0.0309]	21764 R_{int} = 0.040]	20238 [R_{int} = 0.0455]
Completeness to theta max. (%)	30.51°. 99.4%	30.51°. 99.5%	30.51°. 99.9%
Max. and min. transmission	0.9559 and 0.8798	0.9603 and 0.8415	0.6330 and 0.4998
Data / restraints / parameters	10155 / 51 / 533	21764 / 924 / 57	20238 / 140 / 884
Goodness-of-fit on F^2	1.115	1.03	1.030
Final R indices [I>2σ(I)]	R_1 = 0.0676, ωR_2 = 0.1664	R_1 = 0.048, ωR_2 = 0.134	R_1 = 0.0221, ωR_2 = 0.0511
R indices (all data)	R_1= 0.0697, ωR_2 = 0.1673	R_1= 0.0479, ωR_2 = 0.1344	R_1 = 0.0270, ωR_2 = 0.0531
Largest diff. peak and hole	0.509 and −0.678 e.Å^{-3}	1.87 and −1.67 e.Å^{-3}	0.884 and −0.738 e.Å^{-3}

References

[1] D. Tofan, B. M. Cossairt and C. C. Cummins, *Inorg. Chem.*, 2011, **50**, 12349–12358.

[2] D. Tofan and C. C. Cummins, *Chem. Sci.*, 2012, **3**, 2474–2478.

[3] *These data can be obtained free of charge from The Cambridge Crystallographic Data Centre* via *http://www.ccdc.cam.ac.uk/data_request/cif under the Cambridge Structural Database deposition numbers 898619–898621, 898623, 898624, 928307, 928308.*