Electronic Supporting Information (ESI)

for

β-{Cr[RC(CH$_2$O)$_3$]$_2$Mo$_6$O$_{18}$}$^{3-}$: the first organically-functionalized β isomer of Anderson-type polyoxometalates

*Jiangwei Zhang,‡ Yichao Huang,‡ Jian Hao, and Yongge Wei**

Contents

General methods and materials

$[CrMo_6O_{18}(OH)_6]^{3-}$ was synthesized according to literature methods[1]. All syntheses and manipulations were performed in the open air, all other chemicals, including solvents, were commercially available as reagent grade and used as received without further purification from Adamas-beta®. IR spectra were measured using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile by Agilent Cary 300 spectrophotometer. The mass spectra were obtained using an ion trap mass spectrometer (Thermofisher LTQ). Negative mode was chosen for the experiments (capillary voltage 33 V). Sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300 μL min^{-1}. ^{13}C NMR spectra were obtained on a JEOL JNM-ECA400 spectrometer and are reported in ppm. Elemental analyses of C, H, N were performed by Elementar Analysensysteme GmbH (vario EL) while the Elemental analyses of metallic elements were performed by X-ray fluorescence (XRF) element analyzer PANalytical Epsilon 5.

The synthesis of $[TBA]_3[Cr(OH)_6Mo_6O_{18}]$. $(NH_4)_3[Cr(OH)_6Mo_6O_{18}]$ was obtained according to literature methods[1]. Then it was precipitated from the aqueous solution to exchange the counter-cation of $(NH_4)^+$ with TBA^+ by adding equivalent amount of [TBA]Br. $C_{48}H_{114}N_3CrMo_6O_{24}$ M_r = 1745.07, H 6.54 C 32.99 N 2.43 Cr 3.03 Mo 33.02 while calcd H 6.58 C 33.04 N 2.41 Cr 2.98 Mo 32.99. IR (KBr pellet, major absorbance, cm^{-1}): 3152, 1642, 1400, 945, 927, 845, 657. UV-Vis (MeCN, nm): λ_{LMCT} = 238 (ε_{LMCT}=4.66×10^5 L·mol^{-1}·cm^{-1}), λ_{d-d} = 540 (ε_{d-d} = 5.53×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z = 1502.60 $(TBA)_2[Cr(OH)_6Mo_6O_{18}]^-$, 630.06 (TBA) $[Cr(OH)_6Mo_6O_{18}]^{2-}$, 509.33 $[H^+][Cr(OH)_6Mo_6O_{18}]^{2-}$, 339.22 $[Cr(OH)_6Mo_6O_{18}]^{3-}$; found 1502.36,630.12,509.84,339.62, respectively.

The synthesis of compound 1. A mixture of $[TBA]_3[Cr(OH)_6Mo_6O_{18}]$ (1.745 g 1 mmol) with Tris(hydroxymethyl)- aminomethane (0.242 g, 2 mmol) was dissolved in 25 mL hot DMF. After being heated for 12h under nitrogen atmosphere, the reaction solution was cooled down to room temperature to remove the precipitates by filtration and a lavender solution was obtained. Then the filtrate was poured into ether, resulting in precipitation. After the solution became clear, the supernatant liquid was poured off. The product with TBA^+ was obtained as lavender powders (52% yield based on Mo). $C_{56}H_{124}N_5CrMo_6O_{24}$ M_r = 1879.26, H 6.60 C 35.83 N 3.70 Cr 2.80 Mo 30.61 while calcd H 6.65 C 35.79 N 3.73 Cr 2.77 Mo 30.63. IR (KBr pellet, major absorbance, cm^{-1}): 3436, 2962, 2933, 2874, 1637, 1481, 1382, 1115, 1065, 1016, 934, 925, 910, 799, 738, 680. UV-Vis (MeCN, nm): λ_{LMCT} = 222 (ε_{LMCT} =6.74×10^5 L·mol^{-1}·cm^{-1}), λ_{d-d} = 528 (ε_{d-d} = 7.64 ×10^2 L·mol^{-1}·cm^{-1}). ESI mass spectrometry (MeCN): calcd m/z = 1636.79 $(TBA)_2\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 1395.32 $[H^+](TBA)\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 1153.85 $[H^+]_2\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 697.16 (TBA) $\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$, 576.42 $[H^+]\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$, 383.95 $\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{3-}$; found 1637.03, 1395.11, 1153.57, 696.89, 576.56,383.75 respectively. ^{13}C NMR (400 MHz, $[D_6]$ DMSO,

ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 57.8 ($C_ε$), 61.6 (C_a), 64.8 (C_b), 69.7 (C_c), 74.6 (C_d).

The crystallization of compound **1**: $[NH_4]$•β-$\{[H_3NC(CH_2O)_3]_2CrMo_6O_{18}\}$, $C_8H_{22}N_3CrMo_6O_{24}$, M_r = 1171.93. 1 g powder product with TBA^+ were redissolved in 5 mL MeCN, additional 0.1 g of NH_4Cl was dissolved into 1ml 0.1M HCl then added into the crystallization solution to accelerate crystallization process. Single crystals suitable for X-ray diffraction were grown in MeCN solvent by slow evaporation. After crystallization, compound **1** was obtained as lavender crystalline product, which was suitable for single crystal XRD analysis. EA analysis of single crystalline sample of compound **1**, H 1.77 C 8.11 N 3.67 Cr 4.11 Mo 48.88 while calcd H 1.89 C 8.20 N 3.59 Cr 4.44 Mo 49.12

The synthesis of compound 2. The synthesis process is similar to that of compound **1** but using 1,1,1-Tris(hydroxymethyl)-propane (0.268 g, 2 mmol) instead of Tris(hydroxymethyl)aminomethane. The product was obtained as lavender powders (55% yield based on Mo). $C_{60}H_{130}N_3CrMo_6O_{24}$ M_r = 1905.33, H 6.86 C 37.85 N 2.19 Cr 2.75 Mo 30.18 while calcd H 6.88 C 37.82 N 2.21 Cr 2.73 Mo 30.21.IR (KBr pellet, major absorbance, cm^{-1}): 3458, 2961, 2933, 2874, 1647, 1468, 1384, 1118, 1074, 1057, 935, 918, 904, 733, 680. UV-Vis (MeCN, nm): $λ_{LMCT}$ = 220 ($ε_{LMCT}$ = $6.92×10^5$ $L·mol^{-1}·cm^{-1}$), $λ_{d-d}$ = 525($ε_{d-d}$ = $7.77×10^2$ $L·mol^{-1}·cm^{-1}$). ESI mass spectrometry (MeCN): calcd m/z = 1662.86 $(TBA)_2\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 1421.39 $[H^+](TBA)$ $\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^-$, 710.19 $(TBA)\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$, 392.64 $\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^{3-}$; found 1662.66, 1421.77, 710.16, 392.39 respectively. ^{13}C NMR (400 MHz, $[D_6]$ DMSO, ppm): δ = 13.8 ($C_α$), 19.0 ($C_β$), 23.5 ($C_γ$), 57.8 ($C_ε$), 7.9 (C_a), 22.3 (C_b) , 43.8 (C_c), 64.4 (C_d), 69.3 (C_f), 74.1 (C_e).

The crystallization of compound **2**: $[TBA]_2[NH_4]$•$\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}$•$2H_2O$, $C_{44}H_{102}CrMo_6N_3O_{26}$, M_r=1716.93. 1.2 g compound **2** were redissolved in 5 mL MeCN and 3ml H_2O mix solvent, additional 0.1 g of NH_4Cl is added into the crystallization solution to accelerate crystallization process. Single crystals suitable for X-ray diffraction were grown by slow evaporation. After crystallization, compound **2** was obtained as lavender crystalline product. EA analysis of single crystalline sample of compound **2**, H 6.08 C 30.67 N 2.57 Cr 2.78 Mo 33.81 while calcd H 5.99 C 30.78 N 2.45 Cr 3.03 Mo 33.53

Crystallographic data for **1** and **2** are shown in Table S1. Atomic coordinates for the reported crystal structures have been deposited with the Cambridge Structural Database under the accession codes 1447785 and 1447787 for compounds **1** and **2** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

X-ray crystallography

Suitable single crystals were selected. Data collections were performed by graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Agilent Gemini Ultra CrysAlisPro (Ver 1.171.35.11). The structures were solved by direct methods and refined against F^2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All calculations were carried out by the program package of SHELXTL *ver* 5.1 and Olex2 ver 1.2.8.[2,3]

Table S1

Table S1. Crystallographic data for compounds **1**-**2**

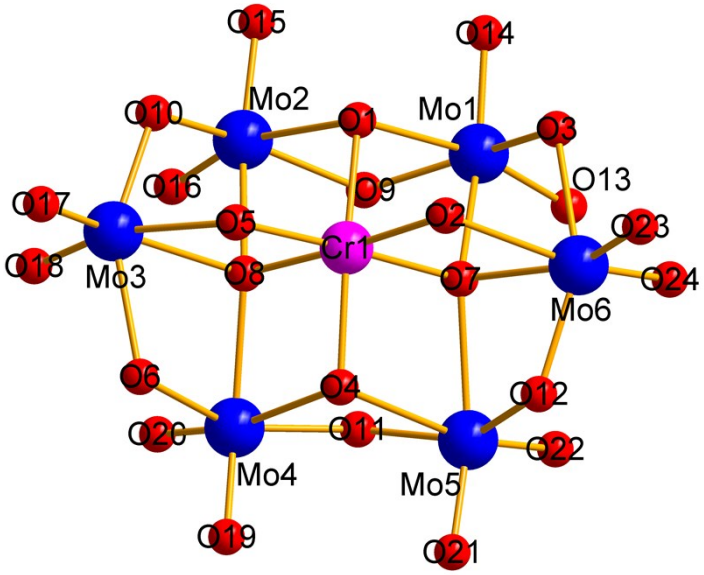
Identification code	**1**	**2**
Empirical formula	$C_8H_{22}N_3CrMo_6O_{24}$	$C_{44}H_{102}CrMo_6N_3O_{26}$
Formula weight	1171.93	1716.93
Temperature (K)	293 (2)	103 (0)
Crystal system	monoclinic	monoclinic
Space group	C2/c	P21/n
a (Å)	26.997(3)	12.8005(4)
b (Å)	17.922(2)v	35.9582(13)
c (Å)	16.364(2)	25.9310(6)
α (°)	90.00	90.00
β (°)	109.860(1)	100.651(3)
γ (°)	90.00	90.00
Volume ($Å^3$)	7446.8(15)	6541.8(4)
Z	8	4
Density ($g.cm^{-3}$)	2.091	1.744
μ (mm^{-1})	2.314	1.351
Crystal size (mm^3)	0.50×0.40×0.30	0.45×0.40×0.20
Reflections collected	7297	12752
Independent reflections	5135	11270
F (000)	4464.0	3436.0
GOF	1.083	1.126
Final R indices [I > 2σ(I)]	R_1=0.0434, wR_2=0.0882	R_1=0.0585, wR_2=0.1084
R indices (all data)	R_1=0.0547, wR_2=0.0987	R_1=0.0606, wR_2=0.1095

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$

[b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

Table S2

Table S2a. Selected bond lengths (Å) of cluster **1**



Selected bond lengths (Å) of cluster **1**			
Cr1-O1	1.969	Mo3-O10	1.895
Cr1-O2	1.959	Mo3-O17	1.726
Cr1-O4	1.966	Mo3-O18	1.712
Cr1-O5	1.946	Mo4-O4	2.296
Cr1-O7	1.975	Mo4-O6	2.097
Cr1-O8	1.985	Mo4-O8	2.146
Mo1-O1	2.284	Mo4-O11	1.902
Mo1-O3	2.061	Mo4-O19	1.709
Mo1-O7	2.142	Mo4-O20	1.700
Mo1-O9	1.902	Mo5-O4	2.326
Mo1-O13	1.741	Mo5-O7	2.244
Mo1-O14	1.706	Mo5-O11	1.934
Mo2-O1	2.340	Mo5-O12	1.951
Mo2-O8	2.205	Mo5-O21	1.689
Mo2-O9	1.951	Mo5-O22	1.696
Mo2-O10	1.982	Mo6-O2	2.207
Mo2-O15	1.719	Mo6-O3	2.130
Mo2-O16	1.684	Mo6-O7	2.189
Mo3-O5	2.207	Mo6-O12	1.890
Mo3-O6	2.093	Mo6-O23	1.736
Mo3-O8	2.194	Mo6-O24	1.719

Table S2b. Selected bond lengths (Å) of cluster **2**.

Selected bond lengths (Å) of cluster **2**			
Cr1-O1	1.981	Cr1-O6	2.010
Cr1-O2	1.965	Cr1-O7	1.996
Cr1-O4	1.969	Cr1-O8	2.020

Table S3

Table S3. Experimental hydrogen bonding interactions of compounds **1**.

	H-Bonds	D−A [Å]	A···H [Å]	D−H···A [°]
1	N3−H3D•••O11	2.883	2.169	150.90
	N3−H3F•••O16	3.002	2.274	152.43
	N3−H3C•••O14	2.888	2.205	138.68
	N1−H1D•••O23	3.444	2.786	131.70
	C6−H6B•••O23	3.284	2.622	125.77

Table S4

Table S4. The UV-Vis data of derivatives of Anderson-type POMs

Compound	LMCT λ_{max} (nm)	d-d transition λ_{max} (nm)
$[TBA]_3[Cr(OH)_6Mo_6O_{18}]$	238	541
1	222	528
2	220	525

Figure S1

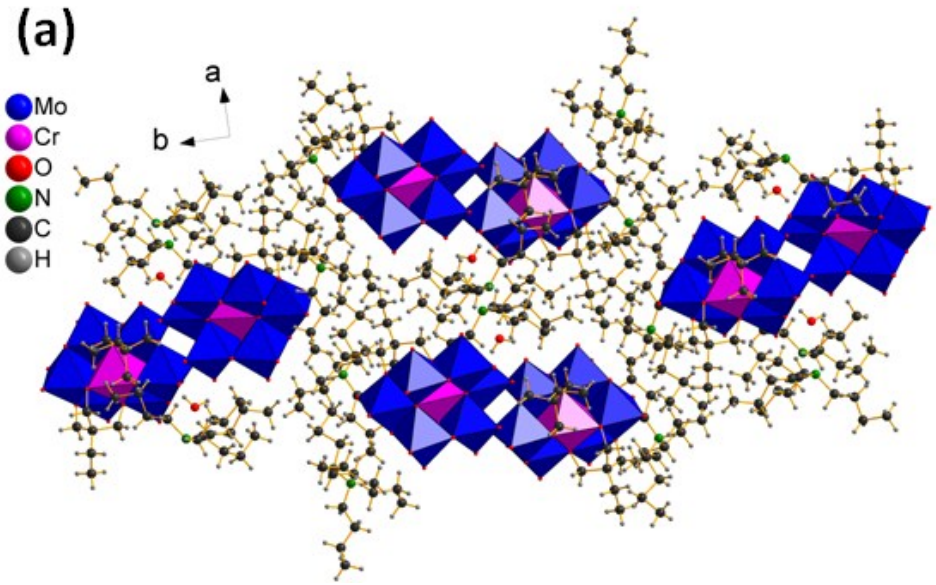


Figure S1. The packing structure of compound **2** along c axis.

Figure S2

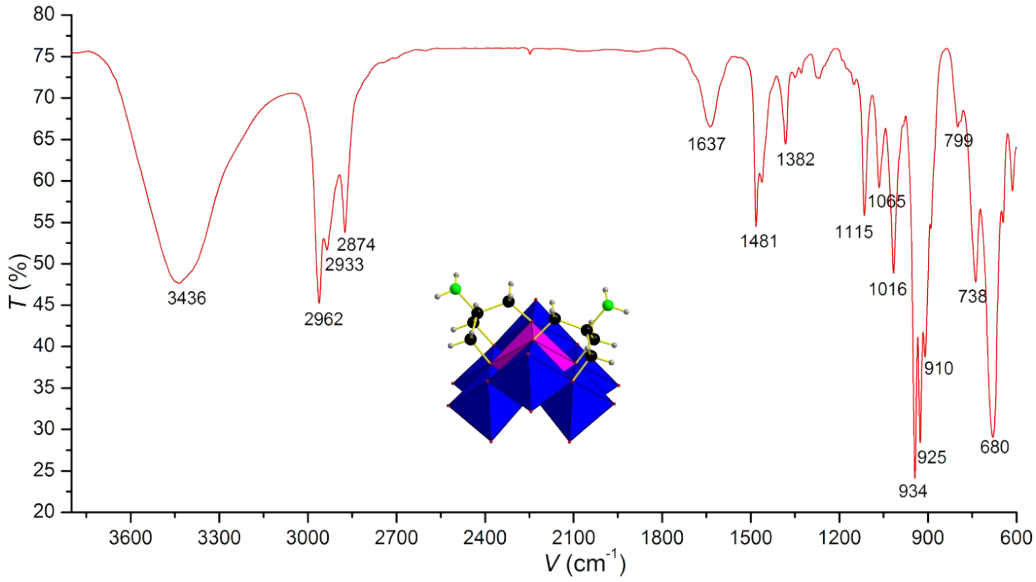


Figure S2a. The IR spectrum of compound **1**.

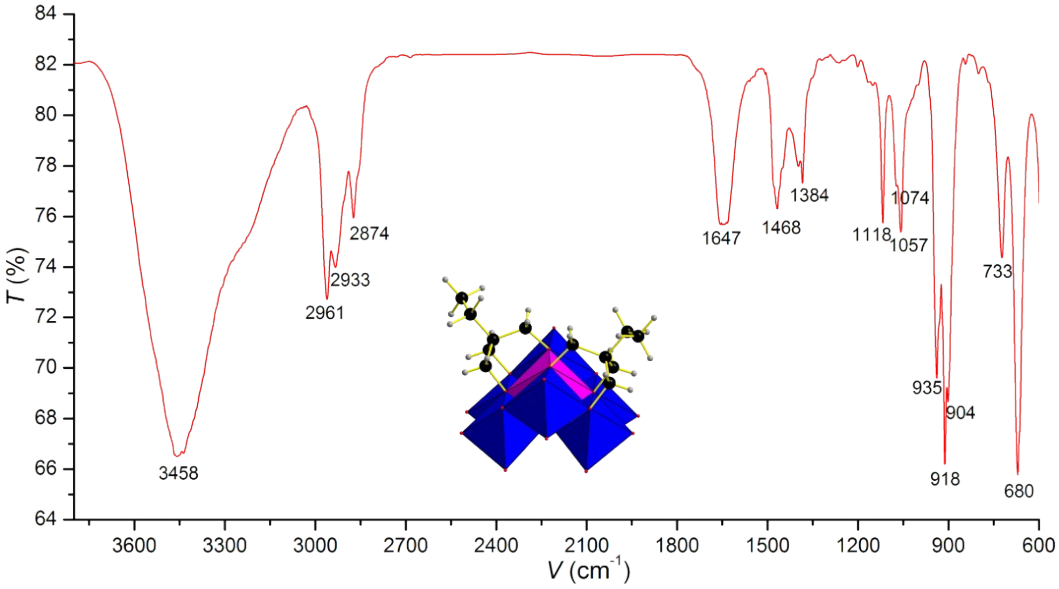


Figure S2b. The IR spectrum of compound **2**.

Figure S3

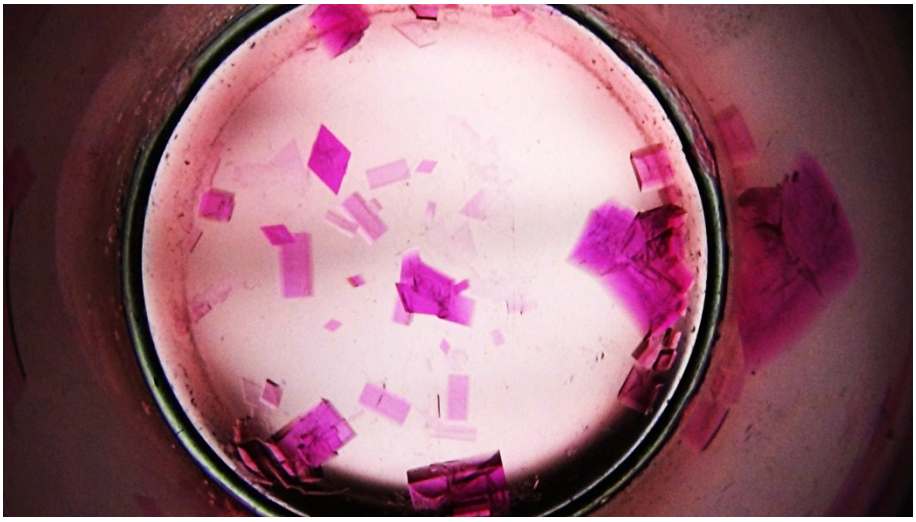


Figure S3. The lavender colour of single crystal of triol-functionalized β-Anderson POM derivative with Cr^{III} central heteroatom, $\{Cr[NH_3C(CH_2O)_3]_2Mo_6O_{18}\}^-$, **1**.

Figure S4

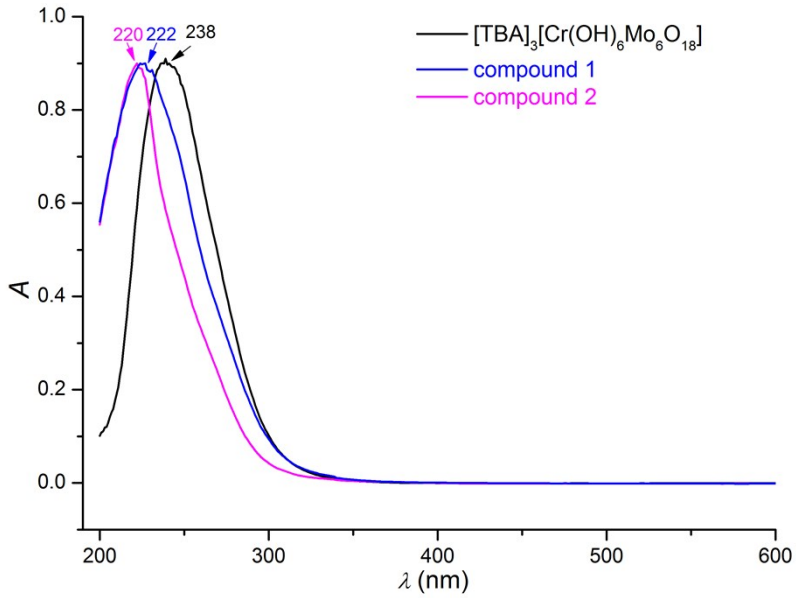


Figure S4a. UV/Vis LMCT spectra of $[TBA]_3[CrMo_6O_{18}(OH)_6]$ and compounds **1** and **2**.

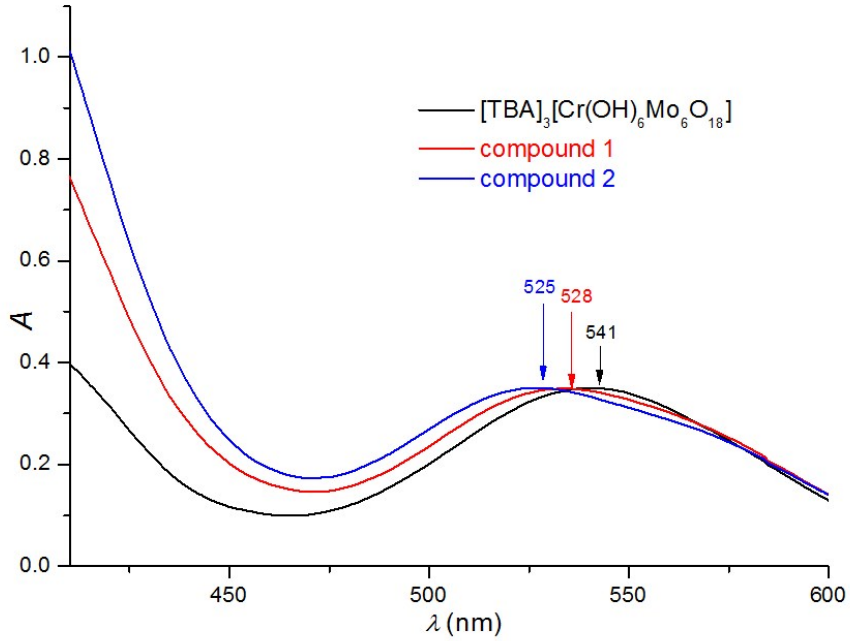


Figure S4b. UV/Vis d-d transition spectra of $[TBA]_3[CrMo_6O_{18}(OH)_6]$ and compounds **1** and **2**.

Figure S5

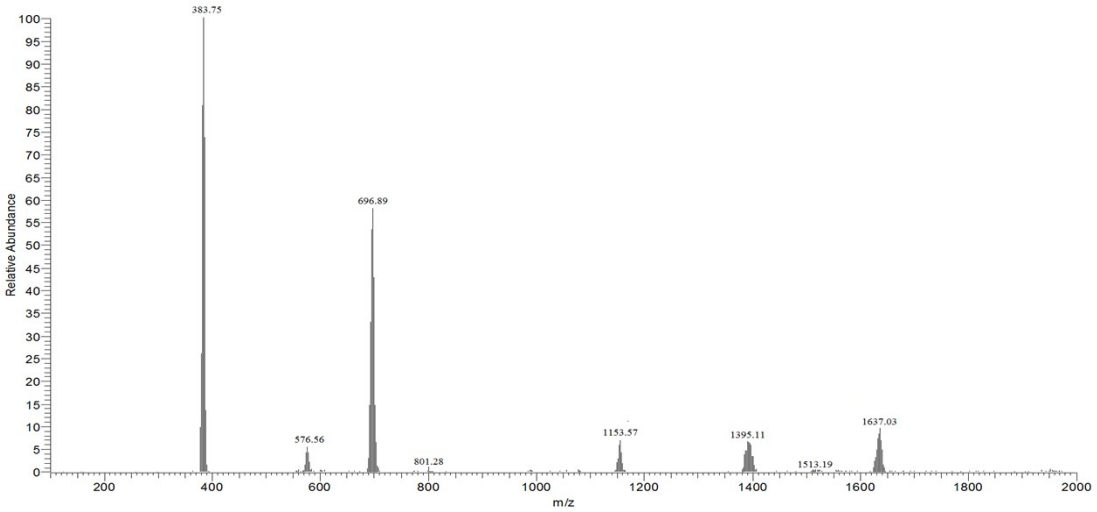


Figure S5a. ESI-MS of compound **1**.

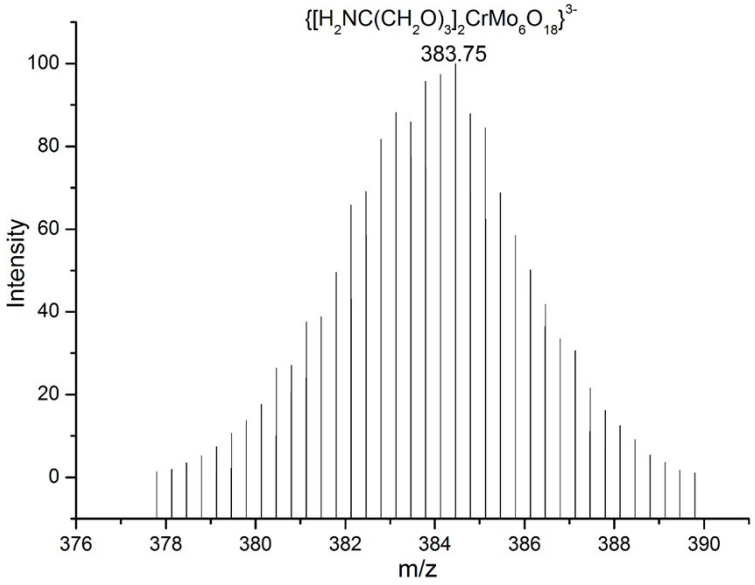


Figure S5b. ESI-MS of compound **1** (100% intensity peak in original size experimental (black) and simulated (red) isotopic patterns)

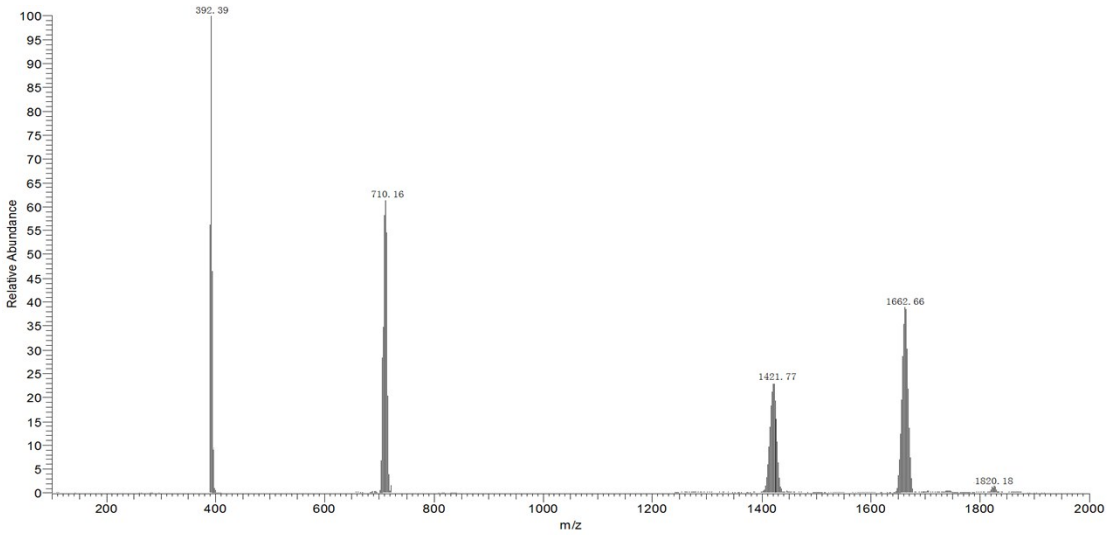


Figure S5c. ESI-MS of compound **2**

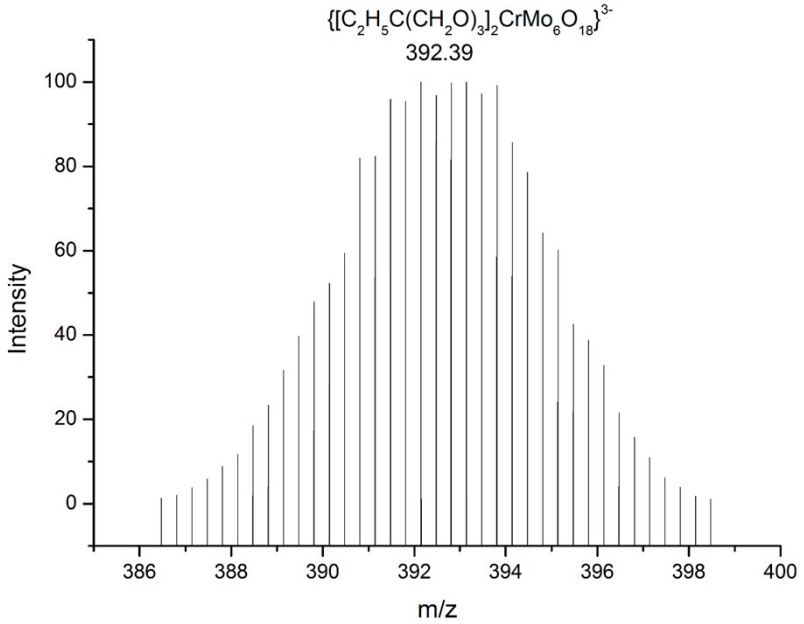


Figure S5d. ESI-MS of compound **2** (100% intensity peak in original size experimental (black) and simulated (red) isotopic patterns)

Table S5

Table S 5a: ESI-MS peak assignments for compound 1:

Peak No.	Recorded m/z	Calculated m/z	Peak assignment
1	1637.03	1636.79	$(TBA)_2\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$
2	1395.11	1395.32	$[H^+](TBA)\ \{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$
3	1153.57	1153.85	$[H^+]_2\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^-$
4	696.89	697.16	$(TBA)\ \{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$
5	576.56	576.42	$[H^+]\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$
6	383.75	383.95	$\{[H_2NC(CH_2O)_3]_2CrMo_6O_{18}\}^{3-}$

Table S 5b: ESI-MS peak assignments for compound 2:

Peak No.	Recorded m/z	Calculated m/z	Peak assignment
1	1662.66	1662.86	$(TBA)_2\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^-$
2	1421.77	1421.39	$[H^+](TBA)\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^-$
3	710.16	710.19	$(TBA)\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^{2-}$
4	392.39	392.64	$\{[C_2H_5C(CH_2O)_3]_2CrMo_6O_{18}\}^{3-}$

Figure S6

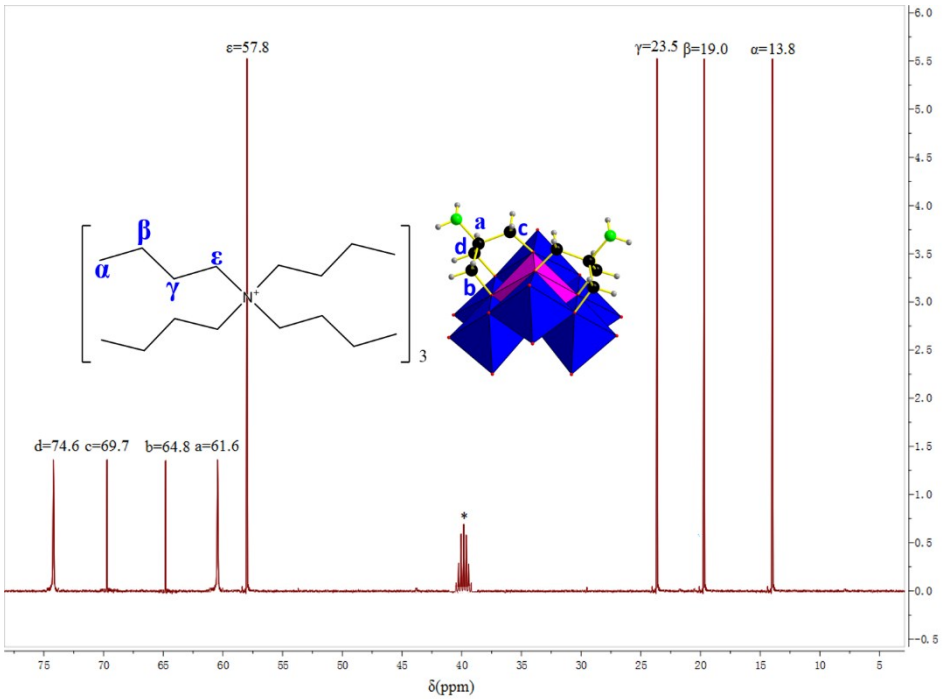


Figure S6a. ^{13}C NMR spectrum of compound **1**

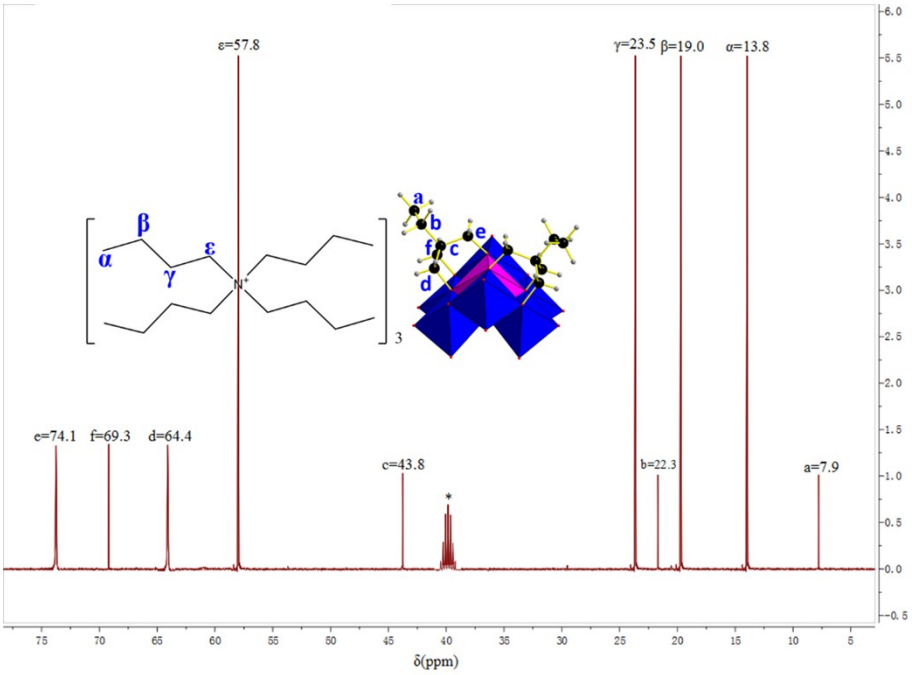


Figure S6b. ^{13}C NMR spectrum of compound **2**

Figure S7

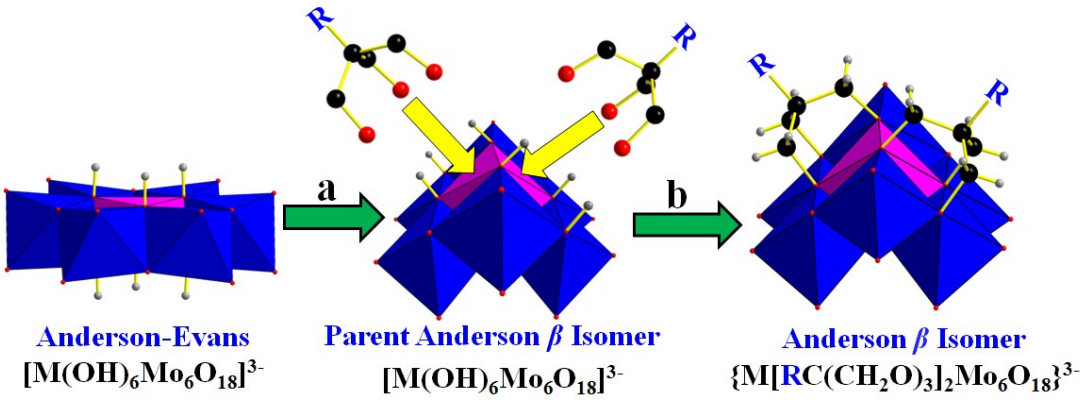


Figure S7. The possible reaction mechanism and the reaction intermediate. a) Isomerization and b) triol functionalization.

DFT calculations details and results

All of the calculations presented herein were carried out with the Gaussian09 program package. The structures of each stationary point were fully optimized by using the B3LYP method, in combination with the LANL2DZ basis set for molybdate and chromium atoms and the 6-31+G(d) basis set for main group elements. The calculation was completed on the "Explorer 100" cluster system of Tsinghua National Laboratory for Information Science and Technology. Details and results of the DFT calculation are briefly presented in the Supplementary Information.

Anderson-Evans $[Cr(OH)_6Mo_6O_{18}]^{3-}$
b3lyp/gen opt freq pop=full int=grid=ultrafine
O H 0
6-31+G(d)
****
Mo Cr 0
LANL2DZ
****
Calculation Type = FREQ
Calculation Method = UB3LYP
Basis Set = Gen
Charge = -3
Spin = Quartet
E(UB3LYP) = -2301.59703696 a.u.
RMS Gradient Norm = 0.00003993 a.u.
Imaginary Freq = 0
Dipole Moment = 0.0000 Debye
Optimization completed Atomic coordinates

O	-0.98536900	-1.37117300	1.05290700
Mo	3.16317200	1.43622700	0.01080300
O	1.67425400	-0.16128900	1.06320700
Mo	-2.82489400	2.02108900	-0.01692700
O	-0.70320700	1.53716400	1.04996600
Mo	0.33793300	3.45755300	-0.00248400
O	1.93365200	2.70839400	0.81278900
O	-3.31646600	0.32514900	0.79296200
O	-1.37192300	3.03004800	-0.81905500
O	-0.11084200	4.55064500	1.25953600
O	0.98850200	4.44513400	-1.26359500
O	-3.98584300	2.18152100	-1.28791900
O	-3.36474900	3.07601000	1.24189700
O	4.33629200	1.37376900	1.27920500

O	-3.89312000	-2.36367200	1.25252000
H	1.60028400	-0.15015800	2.02858400
H	-0.68110700	1.47319700	2.01587100
H	-0.94615000	-1.31387700	2.01868600
O	0.98536900	1.37117300	-1.05290700
O	3.31646600	-0.32514900	-0.79296200
O	3.89312000	2.36367200	-1.25252000
H	0.94615000	1.31387700	-2.01868600
Mo	2.82489400	-2.02108900	0.01692700
O	-1.67425400	0.16128900	-1.06320700
O	0.70320700	-1.53716400	-1.04996600
H	-1.60028400	0.15015800	-2.02858400
H	0.68110700	-1.47319700	-2.01587100
O	1.37192300	-3.03004800	0.81905500
O	3.98584300	-2.18152100	1.28791900
O	3.36474900	-3.07601000	-1.24189700
Mo	-3.16317200	-1.43622700	-0.01080300
Mo	-0.33793300	-3.45755300	0.00248400
O	-1.93365200	-2.70839400	-0.81278900
O	-4.33629200	-1.37376900	-1.27920500
O	0.11084200	-4.55064500	-1.25953600
O	-0.98850200	-4.44513400	1.26359500
Cr	0.00000000	0.00000000	0.00000000

Mulliken charges with hydrogens summed into heavy atoms:

1	O	-0.271951
2	Mo	2.484865
3	O	-0.272253
4	Mo	2.484693
5	O	-0.272166
6	Mo	2.484915
7	O	-1.172416
8	O	-1.172324
9	O	-1.172319
10	O	-0.772012
11	O	-0.771846
12	O	-0.771970
13	O	-0.771761
14	O	-0.771802
15	O	-0.772023
19	O	-0.271951
20	O	-1.172324
21	O	-0.772023
23	Mo	2.484693
24	O	-0.272253

25	O	-0.272166
28	O	-1.172319
29	O	-0.771970
30	O	-0.771761
31	Mo	2.484865
32	Mo	2.484915
33	O	-1.172416
34	O	-0.771802
35	O	-0.772012
36	O	-0.771846
37	Cr	0.020739

Sum of Mulliken charges with hydrogens summed into heavy atoms = -3.00000

Anderson-Evans $\{Cr[H_2NC(CH_2O)_3]_2Mo_6O_{18}\}^{3-}$

b3lyp/gen opt freq pop=full int=grid=ultrafine

C N H O 0

6-31+G(d)

****

Mo Cr 0

LANL2DZ

****

Calculation Type = FREQ

Calculation Method = UB3LYP

Basis Set = Gen

Charge = -3

Spin = Quartet

E(UB3LYP) = -2721.42648753 a.u.

RMS Gradient Norm = 0.00001926 a.u.

Imaginary Freq = 0

Dipole Moment = 0.0030 Debye

Optimization completed Atomic coordinates

Mo	-2.98787000	-1.73453100	-0.00327000
Mo	0.01067200	-3.45118700	-0.00193200
Mo	2.99853200	-1.71617100	0.00628600
C	-0.75805700	-1.27888500	-2.55309400
H	-0.24692200	-2.16016100	-2.96162800
H	-1.77755700	-1.23692400	-2.94619900
O	-0.82671700	-1.43892900	-1.10416200
O	-3.31314000	-0.01057900	-0.83448900
O	-3.62206600	-2.76623800	-1.26435800
O	-0.55369100	-4.50951600	-1.27482700
O	3.63413300	-2.74262400	1.27095100
O	0.57982900	-4.51169100	1.26702600
O	1.66237200	-2.85364800	-0.82632300

O	-1.64331600	-2.86406300	0.82594400
O	0.83359400	-1.43545500	1.10368600
O	0.82687900	1.43866000	1.10438200
O	-0.83371800	1.43533000	-1.10379900
O	1.66589700	0.00409900	-1.08303800
O	-1.66592700	-0.00375700	1.08308100
Mo	2.98826400	1.73462900	0.00301000
Mo	-0.01072400	3.45145600	0.00130500
C	0.75942500	1.27752700	2.55319800
C	0.75832600	-1.27946100	2.55274800
Mo	-2.99869100	1.71614900	-0.00544400
C	-0.76032200	1.27799200	-2.55280200
C	-1.47673700	-0.00025000	2.52747800
C	1.47656200	0.00152900	-2.52743300
O	3.31311400	0.01088800	0.83463200
O	3.62308800	2.76656500	1.26362600
O	4.18329800	1.77026000	-1.27377200
O	1.64354200	2.86417000	-0.82567200
O	0.55335700	4.51076000	1.27352200
O	-0.57997200	4.51110200	-1.26830900
O	-1.66219200	2.85401200	0.82603400
H	0.25013700	2.15924800	2.96309600
H	1.77924400	1.23355600	2.94530000
C	0.00555000	-0.00071000	2.99142200
O	4.19781700	-1.74845200	-1.26658300
H	1.77615400	-1.24006200	2.95047700
H	0.24393300	-2.16105000	2.95648300
O	-4.19691500	1.74756100	1.26842900
O	-3.63563100	2.74288200	-1.26923700
H	-1.77865000	1.23604600	-2.94896400
H	-0.24842900	2.16025500	-2.95825900
C	-0.00575600	0.00022500	-2.99142400
O	-4.18326100	-1.77069800	1.27316700
H	-1.96985900	-0.89303200	2.93186600
H	-1.96794500	0.89553300	2.92750700
H	1.96836900	0.89533300	-2.93112500
H	1.96896800	-0.89324100	-2.92826700
N	0.02919400	-0.00096600	4.47615600
N	-0.02943000	0.00036400	-4.47592600
Cr	0.00004800	0.00007200	0.00001700
H	0.39173700	0.83966300	-4.86863500
H	0.39558800	-0.83692700	-4.86881000
H	-0.39553800	0.83668800	4.86872900
H	-0.39339200	-0.83980600	4.86851000

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	1.453341
2	Mo	1.467202
3	Mo	1.458303
4	C	0.454394
7	O	-0.730073
8	O	-0.764914
9	O	-0.502724
10	O	-0.506866
11	O	-0.511058
12	O	-0.506087
13	O	-0.765751
14	O	-0.764217
15	O	-0.727283
16	O	-0.729746
17	O	-0.727240
18	O	-0.724373
19	O	-0.724742
20	Mo	1.452411
21	Mo	1.466876
22	C	0.449395
23	C	0.390176
24	Mo	1.458619
25	C	0.390792
26	C	0.401863
27	C	0.400955
28	O	-0.765432
29	O	-0.503124
30	O	-0.496421
31	O	-0.764721
32	O	-0.506960
33	O	-0.506329
34	O	-0.765698
37	C	-0.037000
38	O	-0.499468
41	O	-0.499375
42	O	-0.510792
45	C	-0.047455
46	O	-0.496164
51	N	-0.118939
52	N	-0.115184
53	Cr	1.073809

Sum of Mulliken charges with hydrogens summed into heavy atoms = -3.00000

Anderson β isomer $[Cr(OH)_6Mo_6O_{18}]^{3-}$

b3lyp/gen opt freq pop=full int=grid=ultrafine

O H 0

6-31+G(d)

****

Mo Cr 0

LANL2DZ

****

Calculation Type = FREQ

Calculation Method = UB3LYP

Basis Set = Gen

Charge = -9

Spin = Quartet

E(UB3LYP) = -2145.86640270 a.u.

RMS Gradient Norm =0.00002341 a.u.

Imaginary Freq = 0

Dipole Moment = 0.0126 Debye

Optimization completed Atomic coordinates

Mo	1.50215900	2.13155100	-0.82653900
O	1.50392800	0.08890000	-0.18543400
O	-0.07481900	1.95699400	0.81986500
O	1.41373100	3.82742800	-0.62849700
O	-0.12741500	1.74865500	-1.73052500
Mo	-1.78685400	2.03888500	-0.75821500
O	-1.76392400	3.75531000	-0.73292200
O	-1.51882000	-0.07395700	-0.20856100
O	-2.92115800	1.80316600	0.85481300
O	-2.84013100	1.67359000	-2.03693400
Mo	-1.48204900	-2.12418200	-0.84639400
O	0.08480000	-1.92872500	0.82434700
O	-2.67112700	-1.92186300	-2.06142800
O	0.16268000	-1.72597700	-1.74038600
O	-2.72287400	-2.01704500	0.85159200
O	-1.40442300	-3.81162500	-0.57326700
Mo	-3.26760000	-0.02685800	1.11577700
O	-4.42970900	-0.24147900	-0.11631400
O	-1.46705800	-0.15247400	2.37359300
O	-4.16280300	-0.18240400	2.58240700
Mo	1.78878900	-2.05983900	-0.76402500
O	1.75277400	-3.74776800	-0.65087500
O	1.44088600	0.18479800	2.39108400
O	2.71892400	2.06069300	0.84937500
O	2.71491400	1.86235200	-2.04778700
Mo	3.24347000	0.01062200	1.12664100

O	4.17605800	0.18228400	2.57192000
O	2.85940400	-1.80774400	0.85694500
O	4.41487400	0.29042500	-0.09354600
O	2.89963400	-1.70118300	-2.00093400
Cr	-0.00699600	0.00872600	1.09111800
H	0.03747100	-2.51563400	1.58261300
H	-2.60170700	-2.60880700	1.59776200
H	-1.37518800	-0.83865300	3.03859600
H	1.34779500	0.86406700	3.06307700
H	2.58938600	2.63440600	1.60814700
H	-0.04906300	2.52884800	1.59049500

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	0.617053
2	O	-0.385661
3	O	-0.189894
4	O	-0.330749
5	O	-0.338837
6	Mo	0.608128
7	O	-0.326069
8	O	-0.383734
9	O	-0.363048
10	O	-0.301282
11	Mo	0.627847
12	O	-0.192817
13	O	-0.290640
14	O	-0.337455
15	O	-0.184282
16	O	-0.338229
17	Mo	0.580473
18	O	-0.312511
19	O	-0.268450
20	O	-0.354568
21	Mo	0.606101
22	O	-0.325708
23	O	-0.267517
24	O	-0.186768
25	O	-0.293333
26	Mo	0.569772
27	O	-0.353828
28	O	-0.367765
29	O	-0.299250
30	O	-0.288800
31	Cr	0.671820

Sum of Mulliken charges with hydrogens summed into heavy atoms = -3.00000

Anderson β isomer $\{Cr[H_2NC(CH_2O)_3]_2Mo_6O_{18}\}^{3-}$

b3lyp/gen opt freq pop=full int=grid=ultrafine

C N H O 0

6-31+G(d)

****

Mo Cr 0

LANL2DZ

****

Calculation Type = FREQ

Calculation Method = UB3LYP

Basis Set = Gen

Charge = -3

Spin = Quartet

E(UB3LYP) = -2803.56344057 a.u.

RMS Gradient Norm = 0.00001245 a.u.

Imaginary Freq = 0

Dipole Moment = 0.0042 Debye

Optimization completed Atomic coordinates

Mo	-2.11159100	-1.52499800	-1.22725000
O	-1.45354200	0.40577600	-0.57723100
O	-0.56194900	-1.87672800	0.41679200
O	-2.57529000	-3.15954600	-1.03678900
O	-0.44606900	-1.68436500	-2.13276300
Mo	1.03126300	-2.49939800	-1.16499900
O	0.45545700	-4.11662000	-1.14715600
O	1.45992200	-0.41579800	-0.60559800
O	2.18166300	-2.65017500	0.44680600
O	2.14549300	-2.48759300	-2.44418200
Mo	2.08670700	1.53954200	-1.23440000
O	0.54141100	1.85240400	0.43855400
O	3.14625000	0.96998600	-2.45264500
O	0.40108300	1.69788500	-2.12688200
O	3.22727700	1.02947600	0.46065500
O	2.55812100	3.16037400	-0.95375600
Mo	3.10046200	-1.03124000	0.71507500
O	4.26907500	-1.19739700	-0.51835300
O	1.43745200	-0.33708800	1.97697000
O	3.99861500	-1.18001200	2.18060500
Mo	-1.02973400	2.53416200	-1.14587300
O	-0.45068000	4.11953000	-1.02542500
C	0.89501800	2.66110300	1.58513500
O	-1.42366500	0.28237700	1.99871400
C	-1.61564700	-0.70909200	2.97949000

C	-0.87836400	-2.69044400	1.58177000
C	1.63692300	0.66223100	2.96486700
C	3.34311800	1.92892300	1.59161300
H	-0.80151500	-0.79685400	3.49965100
C	-1.98972800	-2.09871000	2.39478400
N	-2.30264000	-3.04753000	3.57863000
H	-0.08692500	-2.77514400	2.13575300
H	-1.13486600	-3.57861300	1.28980700
H	2.32685900	0.35777300	3.57495700
H	0.81799700	0.75848100	3.47582600
C	2.03727600	2.03977400	2.42922100
N	2.29034900	2.97696500	3.59249800
H	-1.58350200	-3.12114800	4.09761500
H	3.58440200	2.81146400	1.26747500
H	4.06014100	1.61933300	2.16639700
H	0.11210300	2.77417700	2.14661300
H	1.16991000	3.54015800	1.27960400
H	1.60599600	2.93633100	4.16021900
H	3.03769100	2.73499400	4.01262400
O	-3.23956900	-1.07312300	0.45134900
O	-3.17305900	-0.87288400	-2.44492100
Mo	-3.07407700	1.03517400	0.73859600
C	-3.33277800	-1.95360100	1.58252000
O	-4.01149200	1.16687700	2.18494600
O	-2.12367200	2.63346100	0.47608600
O	-4.27364300	1.15433300	-0.48049200
H	-3.60606400	-2.83118100	1.27291300
H	-4.02363200	-1.62374100	2.17832100
O	-2.19744700	2.55922000	-2.38214600
H	-2.32044000	-0.42281800	3.58112500
H	-2.97892800	-2.71671900	4.05313700
Cr	0.00294400	-0.01219500	0.69668200

Mulliken charges with hydrogens summed into heavy atoms:

1	Mo	10.545260
2	O	1.392127
3	O	10.329954
4	O	-4.194717
5	O	-5.693932
6	Mo	8.885905
7	O	-3.615617
8	O	1.392127
9	O	-4.469637
10	O	-5.669051
11	Mo	10.545260

12	O	10.329954
13	O	-5.639166
14	O	-5.693932
15	O	-1.401683
16	O	-4.194717
17	Mo	11.277587
18	O	-3.486194
19	O	1.724247
20	O	-5.289248
21	Mo	8.885905
22	O	-3.615617
23	C	0.491306
24	O	1.724247
25	C	1.328220
26	C	0.491306
27	C	1.328220
28	C	-2.460994
30	C	3.274369
31	N	0.058037
36	C	3.274369
37	N	0.058037
45	O	-1.401683
46	O	-5.639166
47	Mo	11.277587
48	C	-2.460994
49	O	-5.289248
50	O	-4.469637
51	O	-3.486194
54	O	-5.669051
57	Cr	-17.773546

Sum of Mulliken charges with hydrogens summed into heavy atoms = -3.00000

Details and results of the BVS calculations

Subroutine Calc_BVS (JRC-LLB, version: March-2005)

Title: Summary of Bond-Valence calculations for file: compound2_cfl.cfl

Atom	Coord	D_aver	Sigm	Distort(x10-4)	Valence	BVSum(Sigma)
Mo1	6.00	1.9694(	39)	112.897	6.000	5.893(67)
Mo2	6.00	1.9765(	42)	140.719	6.000	5.989(87)
Mo4	6.00	1.9726(	46)	126.085	6.000	5.967(90)
Mo6	6.00	1.9743(	41)	105.310	6.000	5.806(78)
Mo3	6.00	1.9658(	41)	105.040	6.000	5.933(82)
Mo5	6.00	1.9713(	44)	154.063	6.000	6.141(83)
Mn1	6.00	1.9629(	41)	0.921	3.000	3.472(38)
O2	4.00	2.0216(	66)	408.360	-2.000	2.053(47)

O8	4.00	2.1372(45)	26.334	-2.000	1.966(24)
O17	1.00	1.6979(129)	0.000	-2.000	1.760(61)
O1	5.00	2.1007(60)	293.463	-2.000	2.138(43)
O10	2.00	1.9412(65)	3.772	-2.000	1.833(32)
O9	2.00	1.9050(64)	2.193	-2.000	2.017(36)
O13	1.00	1.7345(76)	0.000	-2.000	1.594(33)
O12	2.00	1.9217(81)	1.399	-2.000	1.926(41)
O24	1.00	1.7325(129)	0.000	-2.000	1.603(56)
O15	1.00	1.6768(129)	0.000	-2.000	1.863(65)
O7	4.00	2.1323(52)	20.552	-2.000	1.980(29)
O14	1.00	1.7186(93)	0.000	-2.000	1.664(42)
O3	4.00	2.0510(73)	371.792	-2.000	2.092(52)
O6	5.00	2.1108(61)	291.995	-2.000	2.096(45)
O21	1.00	1.6906(92)	0.000	-2.000	1.795(45)
O4	4.00	2.0464(79)	351.479	-2.000	2.067(50)
O16	1.00	1.7296(110)	0.000	-2.000	1.615(48)
O18	1.00	1.7276(95)	0.000	-2.000	1.624(42)
O23	1.00	1.7115(91)	0.000	-2.000	1.696(42)
O22	1.00	1.7006(109)	0.000	-2.000	1.747(52)
O20	1.00	1.7222(109)	0.000	-2.000	1.648(49)
O11	2.00	1.8979(77)	0.732	-2.000	2.052(42)
C4	4.00	2.2639(89)	390.651	4.000	1.018(49)
C2	2.00	1.9651(133)	778.193	4.000	0.985(42)
C1	2.00	1.9564(149)	662.011	4.000	0.907(40)
N1	4.00	2.2329(106)	368.988	-3.000	1.058(49)
C8	4.00	2.2619(89)	396.335	4.000	1.038(46)
C5	2.00	1.9648(163)	677.691	4.000	0.904(46)
C6	2.00	1.9602(128)	728.708	4.000	0.954(41)
N2	4.00	2.2242(103)	371.386	-3.000	1.083(47)
C7	2.00	1.9601(124)	621.971	4.000	0.869(39)
O5	4.00	2.0206(66)	394.558	-2.000	2.039(45)
C3	2.00	1.9586(134)	676.230	4.000	0.915(44)
O19	1.00	1.6932(139)	0.000	-2.000	1.782(67)

References

1 K. Nomiya, T. Takahashi, T. Shirai, M. Miwa, *Polyhedron* 1987, **6**, 213.

2 G. M. Sheldrick, *Acta Crystallogr. A* 2008, **64**, 112.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339.