Supporting information

Proton-Controlled Synthesis of Unprecedented Diol Functionalized Anderson-type POMs

Jiangwei Zhang, Qi Li, Mengyan Zeng, Yichao Huang, Jin zhang, Jian Hao, and Yongge Wei

Experimental Section

General methods and materials
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 Adamsa-beta. \([\text{NH}_4\text{]_2}][\text{CrMo_6O_{18}}(\text{OH})_4]\) were synthesized according to literature methods. IR spectra were measured by using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. UV-Vis spectra were measured in acetonitrile with UV2100s spectrophotometer. The mass spectra were obtained by 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 \(\mu\text{L} \text{min}^{-1}\). Elemental analyses were performed by Elementar Analysetechnik GmbH (vario EL). \(^1\text{C}\) NMR spectra were obtained on a JOEL JNM-ECA400 spectrometer and reported in ppm applying [\(\text{D}_2\text{JMSO}\) as sovlet.

Synthesis and Crystallization process
The synthesis of \([\text{TBA}]_2[[\text{NH}_4\text{C(CH}_2\text{OH})(\text{CH}_2\text{O})_2]\text{CrMo}_6\text{O}_{18}\text{(OH)}_4]\), compound 1:

3.213g \([\text{NH}_4\text{]_2}][\text{CrMo}_{6}\text{O}_{18}\text{(OH)}_4]\) were dissolve in 30ml H\(_2\)O. 0.363g (HOCH\(_2\))\(_2\text{CNH}_2(L_)\) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming \([\text{NH}_4\text{]_2}[[\text{NH}_4\text{C(CH}_2\text{OH})(\text{CH}_2\text{O})_2]\text{CrMo}_6\text{O}_{18}\text{(OH)}_4]\). Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [\(\text{TBA}\)]Br to substitute the \text{NH}_4 cation. The title compound could be obtained as pink crystalline products (75% yields based on Mo).

Compound 1 can be obtained C\(_{20}\)H\(_{22}\)CrMo\(_6\)N\(_2\)O\(_4\) M.\(_r\) = 1831.17, H 6.69 C 34.08 N 3.08 while calcd H 6.72 C 34.11 N 3.06. IR (KBr pellet, major absorbances, cm\(^{-1}\)): 3335, 2961, 2984, 2873, 688. UV-Vis (in MeCN, nm): \(\lambda_{\text{L-MCT}} = 230\text{(c}=10^{-4}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})\), \(\lambda_{\text{d-d}} = 530\text{(c}=10^{-3}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})\times 10^3\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-3}\). ESI mass spectrometry (MeCN): calcd m/z = 1588.62, 1347.49, 1105.84, 863.21 621.13; found 1588.63, 1347.23, 1105.76, 863.12, 621.11.

The crystallization of compound 1: [\(\text{TBA}]_2[[\text{NH}_4\text{C(CH}_2\text{OH})(\text{CH}_2\text{O})_2]\text{CrMo}_6\text{O}_{18}\text{(OH)}_4]\]. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [\(\text{TBA}\)]Br to substitute the \text{NH}_4 cation. The title compound could be obtained as pink crystalline products (75% yields based on Mo).

The synthesis of [\(\text{TBA}]_2[[\text{NH}_4\text{C(CH}_2\text{OH})(\text{CH}_2\text{O})_2]\text{CrMo}_6\text{O}_{18}\text{(OH)}_4]\), compound 2:

3.213g \([\text{NH}_4\text{]_2}][\text{CrMo}_{6}\text{O}_{18}\text{(OH)}_4]\) were dissolve in 30ml H\(_2\)O. 0.357g NH\(_2\text{CH}_{2}\text{CH}_{2}\text{OH}\) (L\(_2\)) were dissolve in 9ml 1M HCl. Then these two solutions were mixed together and refluxing at 100 °C for 3 h forming \([\text{NH}_4\text{]_2}[[\text{NH}_2\text{CH}_{2}\text{CH}_{2}\text{C}O]\text{CrMo}_6\text{O}_{18}\text{(OH)}_4]\). Then it was precipitated from the aqueous by adding equivalent amount of 2.898g [\(\text{TBA}\)]Br to substitute the \text{NH}_4 cation. The title compound could be obtained as pink crystalline products (71% yields based on Mo).

Compound 2 can be obtained C\(_{20}\)H\(_{22}\)CrMo\(_6\)N\(_2\)O\(_4\) M.\(_r\) = 1815.17, H 6.81 C 34.44 N 3.07 while calcd H 6.77 C 34.41 N 3.09. IR (KBr pellet, major absorbances, cm\(^{-1}\)): 3391 2961 2874 1763 1480 1384 1126 1023 938 918 899 661. UV-Vis (in MeCN, nm): \(\lambda_{\text{L-MCT}} = 229\text{(c}=10^{-4}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})\), \(\lambda_{\text{d-d}} = 531\text{(c}=10^{-3}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})\times 10^3\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-3}\). ESI mass spectrometry (MeCN): calcd m/z = 1572.71 1572.62; found 1572.71.

\begin{align*}
  \lambda_{\text{L-MCT}} & = 229\text{(c}=10^{-4}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}) \\
  \lambda_{\text{d-d}} & = 531\text{(c}=10^{-3}\text{ }\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})
\end{align*}
was obtained as pink crystalline products. The synthesis of \([\text{TBA}]\), \(\{\text{CHOH}(\text{CH}_2\text{O})_3\} \text{CrMoO}_3\text{OH}(\text{OH})_2\), compound 3:

3.213g \([\text{NH}_4]\)\text{CrMoO}_3\text{OH}(\text{OH})_2\) were dissolve in 30ml H_2O, 0.276g CHOHO(\text{CH}_2\text{O})_2 \text{L}(\text{L})\) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming \([\text{NH}_4]_3[[\text{CHOH}(\text{CH}_2\text{O})_3] \text{CrMoO}_3\text{OH}(\text{OH})_2]\). Then it was precipitated from the aqueous by adding equivalent amount of 2.898g \([\text{TBA}]\)Br to substitute the \(\text{NH}_4^+\) cation. The title compound could be obtained as pink crystalline products (66% yields based on Mo).

Compound 3 can be obtained \(\text{C}_5\text{H}_{16}\text{BrCrMoO}_5\text{N}_2\text{O}_{25} \text{M}_r = 1802.13\), H 6.69 C 34.04 N 2.30 while calcd H 6.66 C 33.99 N 2.33. IR (KBr pellet, major absorbances, cm⁻¹): 3399 2961 2874 1641 1485 1384 1117 1027 937 916 897 790 737 661. UV-Vis (in MeCN, nm): \(\lambda_{\text{ABS}}=231(\epsilon=10^{-2} \text{Lmol}^{-1} \text{cm}^{-1}), \lambda_{\text{Exc}}=531(\epsilon=10^{-5} \text{Lmol}^{-1} \text{cm}^{-1})\). ESI mass spectrometry (MeCN): calcd m/z=1559.66 \{[\text{TBA}]_2[[\text{CHOH}(\text{CH}_2\text{O})_3] \text{CrMoO}_3\text{OH}(\text{OH})_2]\}, 658.60 \{\text{TBA}\} [[\text{CHOH}(\text{CH}_2\text{O})_2] \text{CrMoO}_3\text{OH}(\text{OH})_2]\}, 537.86 \{[\text{H}]_3[[\text{CHOH}(\text{CH}_2\text{O})_2] \text{CrMoO}_3\text{OH}(\text{OH})_2]\}, 358.24 \{[\text{CHOH}(\text{CH}_2\text{O})_2] \text{CrMoO}_3\text{OH}(\text{OH})_2\}^{-} \text{found} 1559.61, 658.64, 537.89, 358.21 respectively. 

The synthesis of \([\text{TBA}]\), \(\{\text{CHOH}(\text{CH}_2\text{O})_2\} \text{CrMoO}_3\text{OH}(\text{OH})_2\), compound 4:

3.213g \([\text{NH}_4]\)\text{CrMoO}_3\text{OH}(\text{OH})_2\) were dissolve in 30ml H_2O, 0.408g (HOCH_2)C (\text{L})\) were dissolve in 9ml 1M HCl. Then these two solutions was mixed together and refluxing at 100 °C for 3 h forming \([\text{NH}_4]_2[[\text{HOH}2\text{CC}(\text{CH}_2\text{O})_3] \text{CrMoO}_3\text{OH}(\text{OH})_2]\). Then it was precipitated from the aqueous by adding equivalent amount of 2.898g \([\text{TBA}]\)Br to substitute the \(\text{NH}_4^+\) cation. The title compound could be obtained as pink crystalline products (76% yields based on Mo).

The proton-controlled transformation cycling among \(\psi\), \(\delta\) and \(\chi\) isomer and the ultimate proton tolerance of Anderson cluster

3.468g \([\text{NH}_4]\) \(\{\text{NH}_2\text{C}(\text{CH}_2\text{O})_2\} \text{CrMoO}_3\text{OH}(\text{OH})_2\) was obtained following protocol in Scheme 1. Then it was redissolve in 30ml H_2O, 9 ml 1M NaOH was added. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g \([\text{TBA}]\)Br to substitute the \(\text{NH}_4^+\) cation. The pink crystalline products were redissolved in 5% ratio of 60/40 in DMF/McCN mix solvent of 9 ml DMF and 6ml McCN. Additional 0.2 g of \([\text{TBA}]\)Br was added into the crystallization solution to accelerate recrystallization process. After crystallization the \(\delta\) isomer structure of \(\{\text{H}_2\text{NC}(\text{CH}_2\text{O})_2\} \text{CrMoO}_3\text{OH}(\text{OH})_2\}^{-}\) was definitely confirmed as \([\text{TBA}]_2[[\text{H}_2\text{NC}(\text{CH}_2\text{O})_2]\text{CrMoO}_3\text{OH}(\text{OH})_2]\}\{\text{TBA}\}2\text{H}_2\text{O}\) (compound 5). Following the similar process while 6ml 1M NaOH was added instead. Then it was precipitated from the aqueous by adding equivalent amount of 2.898g \([\text{TBA}]\)Br to substitute the \(\text{NH}_4^+\) cation. The pink crystalline products were redissolved in 9 ml DMF and 2ml H_2O mix solvent. After crystallization the \(\chi\) isomer structure of \(\{\text{H}_2\text{NC}(\text{CH}_2\text{O})_2\} \text{CrMoO}_3\text{OH}(\text{OH})_2\}^{-}\) was definitely confirmed as \([\text{TBA}]_2[[\text{H}_2\text{NC}(\text{CH}_2\text{O})_2]\text{CrMoO}_3\text{OH}(\text{OH})_2]\}\{\text{TBA}\}2\text{H}_2\text{O}\) (compound 6). 3.414g \(\text{[NH}_3]_2[[\text{NH}_4\text{C}(\text{CH}_2\text{O})_2]\text{CrMoO}_3\text{OH}(\text{OH})_2]\) was obtained following our previous reported protocol. Then it was redissolve in 24 ml 1M HCl
solution. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898 g [TBA]Br to substitute the NH4+ cation. The yellow precipitate was obtained and further conducted ESI-MS characterization with the confirmation of [MoO4]2− anion formation. 3.363 g χ[NH4]2[NH2C(CH2OH)2] CrMoO4(OH)4 was obtained following our previous reported protocol. Then it was redissolve in 21 ml 1 M HCl solution. The solutions was refluxing at 100 °C for 2 h. Then it was precipitated from the aqueous by adding equivalent amount of 2.898 g [TBA]Br to substitute the NH4+ cation. The yellow precipitate was obtained and further conducted ESI-MS characterization with the confirmation of [MoO4]2− anion formation.

X-ray Crystallographic Structural Determinations

Suitable single crystals were selected. Data collections were performed for compound 1-5 respectively, by using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, ver 2.30). Structures were solved by direct methods and refined against F2 by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. All calculations were carried out by the program package of SHELXTL ver 5.1.2 and Olex2 ver 1.2.7.

DFT calculations

All of the calculations presented herein were carried out with 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. Configuration optimized before Mülliken charge analysis. The calculations were completed on the “Explorer 100” cluster system of Tsinghua National Laboratory for Information Science and Technology.

The solid state IR spectra of compounds 1-3 were similar to each other and they were all in agreement with the typical Anderson-type structures. Herein, we took compound 1 as example, the characteristic peaks at 914, 886 and 836 cm−1 were assigned to the vibrations of terminal Mo=O units and those ones at 783 and 688 cm−1 were definitely confirmed as [TBA]4 [NH4][H2C(CH2OH)2] CrMoO4(OH)4] anion formation. The yellow precipitate was obtained and further conducted ESI-MS characterization with the confirmation of [MoO4]2− anion formation.

Details and results of the DFT calculations


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Mulliken charges with hydrogens summed into heavy atoms:

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Table S1. Selected bond lengths (Å) of the cluster anion for compound 1

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Fig. S1 The single crystals of compound 1
**Fig. S2** ORTEP drawings of cluster anions of χ isomer compounds 4 (left), δ isomer compounds 5 (middle) and χ isomer compounds 6 (right) in the proton-controlled transformation cycling among ψ, δ and χ isomer. Thermal ellipsoids are drawn at the 30% probability level.

**Fig. S3.** ESI mass spectra of substance obtained from δ [NH₄]₃[[NH₂C (CH₂O)₃] CrMo₆O₁₈(OH)₃] refluxing in 12 times stoichiometric ratio of 1M HCl solution at 100 °C for 2 h and precipitated by 3 times stoichiometric ratio of [TBA]Br.

**Fig. S4a** IR spectrum of compound 1.
Fig. S4b IR spectrum of compound 2

Fig. S4c IR spectrum of compound 3
Fig. S4d IR spectrum of compound 4: δ isomers of \( \{[\text{H}_2\text{NC(\text{CH}_2\text{O})}_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^{3-} \)

Fig. S4e IR spectrum of compound 5: χ isomers of \( \{[\text{H}_2\text{NC(\text{CH}_2\text{O})}_3]\text{CrMo}_6\text{O}_{18}(\text{OH})_3\}^{3-} \)
Fig. S5a UV/Vis LMCT spectra of [TBA$_3$][CrMo$_6$O$_{18}$(OH)$_6$] and compound 1

Fig. S5b UV/Vis d-d transition spectra of [TBA$_3$][CrMo$_6$O$_{18}$(OH)$_6$] and compound 1
Fig. S6a The $^{13}$C NMR spectra of compound 1
Fig. S6b The $^{13}$C NMR spectra of compound 2

Fig. S6c The $^{13}$C NMR spectra of compound 3

Fig. S7a ESI mass spectrometry of compound 1
Fig. S7b ESI-MS of compound 1 (100% intensity peak in original size)

Fig. S7c ESI mass spectrometry of compound 2
Fig. S7d. ESI-MS of compound 2 (100% intensity peak in original size)

Fig. S7e. ESI mass spectrometry of compound 3
Fig. S7f ESI-MS of compound 3 (100% intensity peak in original size)
**Fig S.9** The stoichiometric ratio proton introduced served as a key option to control whether the $\psi$, $\delta$, or $\chi$ isomer will be generated.

**Reference:**