Electronic Supporting Information (ESI) for

$[V_4Mo_3O_{14}(NAr)_3(\mu_2-NAr)_3]^{2-}$: the First Polyarylimido-Stabilized Molybdovanadate Cluster

Yichao Huang, Jiangwei Zhang, Jingxuan Ge, Chong Sui, Jian Hao,* and

Yongge Wei*

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Contents

General methods and materials

All syntheses and manipulations were performed under N₂ gas. All other chemicals, including solvents, were commercially available as reagent grade from Adamas-beta®. [TBA]₄[Mo₈O₂₆] and [TBA]₃[V₁₀O₂₈H₃] were synthesized according to literature methods¹ and dried before use. The aniline was also dried before use. Acetonitrile was dried by refluxing in the presence of CaH₂ and was distilled prior to use. *N*, *N'*-Dicyclohexylcarbodiimide (DCC), was used directly without further purification. 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), and sample solution (in acetonitrile) was infused into the ESI source at a flow rate of 300 μ L min⁻¹. Elemental analyses were performed by Elementar Analysensysteme GmbH (vario EL). ¹H NMR was obtained on a JEOL JNM-ECA600 spectrometer and reported in ppm. ¹³C NMR

Synthesis of compound 1a and Mo5V1. 2.153 g [TBA]₂[Mo₈O₂₆] (1 mmol), 0.844 g [TBA]₃[V₁₀O₂₈H₃] (0.5 mmol), 1.677 g aniline (18 mmol) and 4.127 g DCC (20mmol) were dissolved in 50mL anhydrous MeCN, then the solution was refluxing at 80 °C. After 12 h, the reaction solution was filtrated to isolate the white precipitates of 1, 3-dicyclohexylurea (DCU) and 1,3-dicyclohexylguanidine, and then the filtrate was poured into ether, resulting in precipitation. After the solution became clear, the supernatant liquid was poured off. Then aceton (BT) was added to the residue, leading to deep-purple solution and some yellow powder. The yellow powder was isolated by filtration and then dissolved in anhydrous MeCN, which was transfered into a bottle with diethyl ether (Et₂O). After slow gaseous diffusion and crystallization, yellow crystals of (TBA)₃[Mo₅V₁O₁₉] (**Mo5V1**) in modest yield (42%) could be obtained. Compound Mo5V1: IR (KBr pellet, major absorbances, cm⁻¹): 2958, 2873, 1480, 1381, 1151, 1026, 976, 930, 883, 788. UV-Vis (MeCN, nm): $\lambda_1 = 240$, $\lambda_2 = 262$, $\lambda_3 = 319$. ESI-MS (m/z, MeCN): calcd. for (TBA)₂[Mo₅V₁O₁₉]⁻, 1319.56; (TBA)₁H[Mo₅V₁O₁₉]⁻, 1078.10; found, 1320.93, 1077.65 respectively. Elemental analysis (calcd., found for $C_{48}H_{108}Mo_5N_3O_{19}V_1$, $M_r = 1562.02$): C (36.91, 36.87), H (6.97, 6.95), N (2.69, 2.65). The deep-purple solution was transferred into a bottle with ether and set aside. Black needle crystals of $(TBA)_2[V_4Mo_3O_{14}(NAr)_3(\mu_2-$ NAr)₃] (1a) were obtained in a yield of approximately 46% from the BT-Et₂O filtrate within a few days. Compound **1a**: ¹H NMR (600 MHz, DMSO-d6, ppm): δ = 0.94 (t, 24H, TBA-H), 1.33 (sextet, 16H, TBA-H), 1.57 (quintet, 16H, TBA-H), 3.17 (t, 16H, TBA-H), 6.13 (d, 6H, Ar-H), 6.58 (d, 6H, Ar-H), 6.72 (t, 3H, Ar-H), 6.88 (t, 3H, Ar-H), 6.94 (t, 6H, Ar-H), 7.05 (t, 6H, Ar-H). ¹³C NMR (400 MHz, DMSO-d6, ppm): 14.11, 20.48, 24.66, 59.29, 118.91, 124.05, 127.02, 127.79, 128.02, 128.38, 152.67, 169.73. IR (KBr pellet, major absorbances, cm⁻¹): 3057, 2959, 2870, 1578, 1473, 1319, 1243, 1154, 1024, 981, 972, 952, 906, 826, 783, 760, 683. UV-Vis (DMF, nm): λ_1 = 228, λ_2 = 335. ESI-MS (m/z, DMF): calcd. for (TBA)₁[Mo₃V₄O₁₄(NC₆H₅)₆]⁻, 1504.72; [Mo₃V₄O₁₄(NC₆H₅)₆]²⁻, 631.12; found, 1503.93, 630.83 respectively. Elemental analysis (calcd., found for C₆₈H₁₀₂Mo₃N₈O₁₄V₄, M_r =1747.19): C (46.75, 46.78), H (5.88, 5.91), N (6.41, 6.39).

Synthesis of compound 1b and 1c. $(G)_2[V_4Mo_3O_{14}(NAr)_3(\mu_2-NAr)_3] \cdot H_2O$ (G = $C_6H_5NHC(NHC_6H_{11})_2$, **1b**) was synthesized in the similiar reaction conditions as compound **1a**, except that addictional 0.26 g aniline hydrochlorides (2 mmol) were added into the reaction. After 6 hours, the reaction solution was filtrated and the the filtrate was set aside at room temperature to remove the MeCN solvents. Small black rod-like crystals of compound **1b** could be obtained with a yield of about 15% after two days. Compound **1c** $(G)_2[V_4Mo_3O_{14}(NAr)_3(\mu_2-NAr)_3] \cdot 2DMF$ (**1c**) was obtained by recrystallization of compound **1b** in DMF solution for two weeks. Compounds **1b** and **1c**

have the same structures, except that compounds 1b contains H₂O molecules as cocrystal-solvent while compound 1c contains DMF molecules as cocrystal-solvent. Compound **1b**: ¹H NMR (600 MHz, DMSO-d6, ppm): δ = 1.09 (t, 8H, Cy-H), 1.30 (sextet, 16H, Cy-H), 1.73 (sixtet, 16H, Cy-H), 6.13 (d, 6H, Ar-H), 6.59 (d, 6H, Ar-H), 6.74 (t, 3H, Ar-H), 6.85-6.99 (m, 9H, Ar-H), 7.05 (t, 6H, Ar-H), 7.22 (t, 2H, G-Ar-H), 7.42 (t, 4H, G-Ar-H), 7.58 (t, 4H, G-Ar-H). IR (KBr pellet, major absorbances, cm⁻¹): 3230, 3056, 2928, 2851, 1633, 1581, 1474, 1446, 1352, 1315, 1242, 1068, 974, 907, 829, 782, 762, 685. UV-Vis (MeCN, nm): λ_1 = 229, λ_2 = 335. ESI-MS (m/z, DMF): calcd. for $(G)_{1}[Mo_{3}V_{4}O_{14}(NC_{6}H_{5})_{6}]^{-}, 1562.72; [Mo_{3}V_{4}O_{14}(NC_{6}H_{5})_{6}]^{2-}, 631.12; found, 1562.81, 630.83$ respectively. Elemental analysis (calcd., found for C₇₄H₉₂Mo₃N₁₂O₁₅V₄, M_r =1881.18): C (47.25, 47.26), H (4.93, 4.91), N (8.93, 8.89). Compound 1c: IR (KBr pellet, major absorbances, cm⁻¹): 3056, 2928, 2849, 1663, 1581, 1474, 1444, 1386, 1319, 1253, 1151, 1091, 1025, 973, 907, 826, 781, 757, 683, 659. UV-Vis (DMF, nm): $\lambda_1 = 228$, $\lambda_2 = 335$. ESI-MS (m/z, DMF): calcd. for (G)₁[Mo₃V₄O₁₄(NC₆H₅)₆]⁻, 1562.72; [Mo₃V₄O₁₄(NC₆H₅)₆]²⁻, 631.12; found, 1562.81, 630.83 respectively. Elemental analysis (calcd., found for C₈₀H₁₀₄Mo₃N₁₄O₁₆V₄, M_r =2009.35): C (47.82, 47.84), H (5.22, 5.21), N (9.76, 9.74).

Crystallographic data for **1a**, **1b**, **1c** and **Mo5V1** are shown in Table S1. CCDC - 1033547 (**1a**), 1519445 (**1b**), 1519446 (**1c**) and 1513602 (**Mo5V1**) contain the supplementary crystallographic data for this paper. 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-K α radiation ($\lambda = 0.71073$ Å). Data reduction, cell refinement and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, ver 2.30). 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

Table S1

Identification code	1a	1b	1c	Mo5V1
Empirical formula	C ₆₈ H ₁₀₂ Mo ₃ N ₈ O ₁₄ V ₄	$C_{74}H_{92}Mo_3N_{12}O_{15}V_4$	C ₈₀ H ₁₀₄ Mo ₃ N ₁₄ O ₁₆ V ₄	C ₄₈ H ₁₀₈ Mo ₅ N ₃ O ₁₉ V ₁
Formula weight	1747.16	1881.17	2009.35	1561.97
Temperature (K)	98.00 (5)	173.00 (10)	173.00 (10)	103
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	C2/c
a (Å)	13.4643(7)	12.4632(4)	12.5610(3)	29.2304(18)
b (Å)	16.5903(11)	14.0872(4)	14.4766(4)	18.5275(10)
c (Å)	21.0115(14)	26.2550(8)	25.9310(6)	27.1217(13)
α (°)	107.438(6)	104.468(2)	103.598(2)	90.00
β (°)	92.843(5))	96.532(2)	96.5613(17)	113.089(7)
γ (°)	108.583(5)	104.992(3)	105.634(2)	90.00
Volume (Å ³)	4189.3(4)	4232.4(2)	4333.34(19)	13511.6(15)
Z	2	2	2	8
Density (g.cm ⁻³)	1.385	1.476	1.540	1.536
µ (mm ⁻¹)	0.919	7.615	7.493	1.095
Crystal size (mm ³)	0.40×0.15×0.1	0.60×0.30×0.20	0.50×0.30×0.30	0.40×0.35×0.33
Reflections collected	36311	30037	32458	31155
Independent	16442	17221	17728	13297
reflections				
F (000)	1792.0	1916.0	2056.0	6415.8
GOF	1.026	1.048	1.050	1.039
Final R indices [I >	R ₁ =0.0424,	R ₁ =0.0918,	R ₁ =0.0398,	R ₁ =0.0644,
2σ(I)]	wR ₂ =0.0975	wR ₂ =0.2376	wR ₂ =0.1046	wR ₂ =0.1497
R indices (all data)	R ₁ =0.0584,	R ₁ =0.1290,	R ₁ =0.0435,	R ₁ =0.1080,
	wR ₂ =0.1011	wR ₂ =0.2609	wR ₂ =0.1084	wR ₂ =0.1800
${}^{a}R_{1} = \Sigma F_{o} - F_{c} / \Sigma F_{o} $				
${}^{b}wR_{2} = \{\Sigma[w(F_{o}^{2}-F_{c}^{2})^{2}$]/Σw(F _o ²) ² } ^{1/2}			

Table S1. Crystallographic data for compounds 1a, 1b, 1c and Mo5V1

Table S2

Selected bond lengths (Å) of cluster 1				
Mo1-O1	2.085	V1-O1	3.022	
Mo2-O1	2.094	V2-O1	3.039	
Mo3-O1	2.105	V3-O1	3.057	
		V4-O1	3.437	

 Table S2a. Selected bond lengths (Å) of cluster 1 (Take compound 1a for example)

Table S2b. Selected bond lengths (Å) of cluster 1.

Selected bond lengths (Å) of cluster 1			
Mo1-N1	1.763	Mo2-N4	2.065
Mo2-N2	1.760	Mo2-N5	1.953
Mo3-N3	1.755	Mo3-N5	2.080
Mo1-N4	1.964	Mo3-N6	1.961
Mo1-N6	2.072		
 Ta	able S2c. Selected an	igles (°) of the cluster 1 .	
Selected angles (°) of cluster 1			
Mo1-N1-C1	172.821	Mo1-N4-C19	128.594
Mo2-N2-C7	172.355	Mo1-N6-C31	125.528
Mo3-N3-C13	175.491	Mo3-N5-C25	120.923
Mo2-N5-C25	128.825	Mo3-N6-C31	125.528
Mo2-N4-C19	125.681		
Table S2d. Selected torsion angles(°) of the cluster 1.			
	Selected torsion ar	igles (°) of cluster 1	
Mo1-N6-C31-C32	63.211	Mo3-N5-C25-C30	58.340
Mo2-N4-C19-C24	59.021		

Table S3

	H-Bonds	D-A [Å]	A…H [Å]	D−H…A [°]
1b	N7-H7•••O5	2.794	1.994	154.22
	N8-H8A•••O4	3.085	2.424	134.20
	N9-H9A•••O9	2.919	2.072	168.02
	N10-H10A•••O15	2.819	2.037	150.86
	N11-H11A•••O3	2.796	1.963	162.75
	N12-H12A•••O2	2.970	2.171	154.43
	O15-H15A•••O6	2.904	2.468	112.72
1c	N7-H7•••O15	2.714	1.939	149.38
	N8-H8A•••O5	2.933	2.154	150.46
	N9-H9A•••O4	2.766	1.911	172.29
	N10-H10A•••O2	2.793	2.006	151.83
	N11-H11A•••O9	2.937	2.082	172.54
	N12-H12A•••O3	3.095	2.472	129.88

 Table S3. Experimental hydrogen bonding interactions of compounds 1b and 1c.

Table S4

Compound	Lable	λ _{max} (nm)
[M0 ₆ O ₁₉] ²⁻	Mo6	325
[Mo ₆ O ₁₈ (NAr)] ²⁻	1-Ar'	351
[Mo ₆ O ₁₇ (NAr) ₂] ²⁻	2-Ar'- <i>cis</i>	356
[Mo ₆ O ₁₆ (NAr) ₃] ²⁻	3-Ar'-l	361
[Mo ₆ O ₁₅ (NAr) ₄] ²⁻	4-Ar'-I	364
[Mo ₆ O ₁₄ (NAr) ₅] ²⁻	5-Ar'-l	364
[Mo ₆ O ₁₆ (NAr) ₂ (µ ₂ -NAr)] ²⁻	3-Ar-III	353
$[Mo_6O_{14}(NAr)_4(\mu_2-NAr)]^{2-1}$	[5-Ar-l][5-Ar-ll]	365
$[Mo_6O_{13}(NAr)_3(\mu_2-NAr)_3]^{2-1}$	Mo6-6NAr	329
[V ₄ Mo ₃ O ₁₄ (NAr) ₃ (µ ₂ -NAr) ₃] ²⁻	1a, 1b, 1c	335

TableS4. The UV-Vis data of some substituted derivatives of POMs and $[Mo_6O_{19}]^{2-.3-5}$



Figure S1. (a), (b) and (c) Experimental (black) and simulated (red) isotopic patterns for $H\{1\}^{-}$, TBA₁ $\{1\}^{-}$ and (TBA)₂ $\{Mo5V1\}^{-}$ respectively (the calcd m/z value corresponding to the highest isotopic peak was shown).



Figure S2a. ORTEP drawing of cluster 1 (compound 1a). Termal ellipsoids are drawn at the 50% probability level.



Figure S2b. ORTEP drawing of compound 1b. Termal ellipsoids are drawn at the 50% probability level.



Figure S2c. ORTEP drawing of compound 1c. Termal ellipsoids are drawn at the 50% probability level.



Figure S3. Crystal structures of cluster **1** in compound **1a**. a) Packing along *a* axis (drawn by space filling). b) Packing along *b* axis (drawn by space filling). c) and d) Dimeric unit of cluster **1** (drawn by ball and stick and polyhedron, the green dotted lines show the intermolecular C-H... π interactions). Colour code for a) and b) : Mo, indigo blue; V, purple; O, red; N, sky blue; C, gray; H, white.



Figure S4a. Hydrogen bonding interactions in compound **1b** (represented in polyhedron, ball and stick mode, hydrogen bonds are drawn as green dotted lines)



Figure S4b. Supermolecule structure of compound **1b** formed by H-bonding interations. Hydrogen donds are drawn as orange dotted lines.



Figure S5a. Hydrogen bonding interactions in compound **1c** (represented in polyhedron, ball and stick mode, hydrogen bonds are drawn as green dotted lines)



Figure S5b. Superamolecule structure of compound **1c** formed by H-bonding interations. Hydrogen donds are drawn as orange dotted lines.





Figure S6d. The 1 H NMR spectrum of compound 1b.



Figure S7a. The IR spectrum of compound 1a.



Figure S7b. The IR spectrum of compound 1b.







Figure S8a. UV/Vis absorption spectra of compound 1a in DMF solution.



Figure S8b. UV/Vis absorption spectra of compound 1b in DMF solution.



Figure S8c. UV/Vis absorption spectra of compound 1c in DMF solution.



Figure S9b. The ESI-MS of compound 1a (100% intensity peak in original size).



Figure S9d. The ESI-MS of compound 1b (100% intensity peak in original size).



Figure S9f. The ESI-MS of compound 1c (100% intensity peak in original size).

Interestingly, yellow crystals of Mo5V1 in modest yield (42%) were also obtained as by-products during the purification of compound 1a. Crystallographic analysis revealed Mo5V1 to be isostructural with Lindqvist-POM cluster, crystallizing in the monoclinic space group C2/c (Table S1), which has been reported by Klemperer and Howarth *et al.*⁶ The V atom and Mo atoms are randomly disordered at all metal sites in the Mo5V1 crystal. Combined with the single crystal XRD result and ESI-MS result, the Mo : V ratios should be 5 : 1. Indeed, detailed studies of molybdovanadates with different Mo : V ratios have been well established in aqueous solution at different pH values by Klemperer and Howarth *et al.* Here, a novel non-aqueous approach for the synthesis of molybdovanadates has also been reported.



Figure S10a. a) Ball and stick representation of $[Mo_5V_1O_{19}]^{3-}$ (Mo5V1); b) Polyhedral representation of $[Mo_5V_1O_{19}]^{3-}$ (Mo5V1).



Figure S10b. UV/Vis absorption spectra of Mo5V1 in MeCN solution.



Figure S10c. The IR spectrum of compound Mo5V1.



Figure S11b. The ESI-MS of Mo5V1 (100% intensity peak in original size).

References

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