Supporting Information

Stability and Structure in α - and β -Keggin Heteropolytungstates, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$, X = p-Block Cation

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List of Tables, Discussion, and Experimental Procedures:

Tables:

Table S1. Comprehensive Annotated Catalogue of 142 Keggin Heteropolytungstates Structurally Characterized by X-ray Crystallography

Table S2. Crystal Data and Structure Refinement for β -Cs_{4.5}K_{0.5}1

Table S3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for β -Cs_{4.5}K_{0.5}1

Table S4. Selected Bond Distances (Å) and Angles (deg) for β -Cs_{4.5}K_{0.5}1 (Molecule 1)

Table S5. Selected Bond Distances (Å) and Angles (deg) for β -Cs_{4.5}K_{0.5}1 (Molecule 2)

Table S6. Crystal Data and Structure Refinement for β -Cs_{3.5}K_{1.5}1

Table S7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for β -Cs_{3.5}K_{1.5}1

Table S8. Selected Bond Distances (Å) and Angles (deg) for β -Cs_{3.5}K_{1.5}1

Table S9. Crystal Data and Structure Refinement for β -K₅1

Table S10. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for β -K₅1

Table S11. Selected Bond Distances (Å) and Angles (deg) for β -K₅1

Table S12. Mean Distances (Å) and Angles (deg) from Crystallographic Data Acquired using Crystals of Three Different β -[AlW₁₂O₄₀]⁵⁻ Salts

Additional Discussion:

1. Evaluation of previously reported crystal structures of β -[SiW₁₂O₄₀]⁴⁻.

Experimentals:

2. Preparation of X-ray quality crystals of β -Cs_{4.5}K_{0.5}1.
3. Preparation of X-ray quality crystals of β -Cs_{3.5}K_{1.5}1.
4. Preparation of X-ray quality crystals of β -K₅1.
5. X-ray crystallographic studies: Methods and refinement.

Table S1. Keggin Heteropolytungstates Structurally Characterized by X-ray Crystallography (Comprehensive Annotated Catalogue of 142 Solved Structures)

No.	POM Salt (counter cations and anion) Comments: Disorder, apparent incongruities in atomic coordinates, partial-occupancy refinements, and whether atomic coordinates are available. Reference: Journal and/or Cambridge Structural Database (CSD; April, 2002) or Inorganic Crystal Structure Database (ICSD; August 2001) reference codes.
1	$\alpha\text{-K}_6[\text{Co}^{\text{II}}(\text{OH}_2)_6]_{0.5}[\text{AlCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 11\text{H}_2\text{O}$ Terminal aqua ligands on Co atoms assumed for charge balance Cowan, J. J.; Bailey, A. J.; Heintz, R. A.; Do, B. T.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. <i>Inorg. Chem.</i> 2001 , 6666. Submitted to ICSD in 2002.
2	$\alpha\text{-K}_6[\text{AlMn}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 16\text{H}_2\text{O}$ Terminal aqua ligand on Mn assumed for charge balance Cowan, J. J.; Bailey, A. J.; Heintz, R. A.; Do, B. T.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. <i>Inorg. Chem.</i> 2001 , 6666. Submitted to ICSD in 2002.
3	$\alpha\text{-K}_5[\text{Al}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 7\text{H}_2\text{O}$ Weinstock, I. A.; Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. <i>J. Am. Chem. Soc.</i> 1999 , 4608. Submitted to ICSD 2002.
4	$\beta\text{-Cs}_{4.5}\text{K}_{0.5}[\text{AlW}_{12}\text{O}_{40}]\cdot 7.5\text{H}_2\text{O}$ This work
5	$\beta\text{-Cs}_{3.5}\text{K}_{1.5}[\text{AlW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$ This work
6	$\beta\text{-K}_5[\text{AlW}_{12}\text{O}_{40}]\cdot 3\text{H}_2\text{O}$ This work
7	$\alpha\text{-Ba}_3[\text{B}^{\text{III}}\text{Co}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 26\text{H}_2\text{O}$ Disordered BO_4 ; Co disordered over 12 positions (0.083 Co/0.917 W); some Ba counter-cations refined with partial occupancy; deformed at O(3) (possibly wrong coord.); terminal aqua ligand on Co assumed for charge balance Weakley, J. R. <i>Acta Cryst. C</i> 1984 , 16. ICSD ID: 48113.
8	$\alpha\text{-Cs}_3\text{H}_2[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot \text{H}_2\text{O}$ Coord. not available; H counter-cations assumed for charge balance Santos, J. A. <i>Proc. Royal Soc. London, Ser. A: Math. and Phys. Sci.</i> 1935 , 309. ICSD ID: 33116.
9	$\alpha\text{-}[\text{NH}_4]_5[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 26\text{H}_2\text{O}$ Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1935 , 402. ICSD ID: 38517.
10	$\alpha\text{-K}_5[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$ Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38539.
11	$\alpha\text{-H}_5[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 14\text{H}_2\text{O}$ Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1939 , 394. ICSD ID: 38588.
12	$\alpha\text{-}[\text{C}_{10}\text{H}_8\text{S}_8]_6[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 2\text{C}_{10}\text{H}_8\text{S}_8\cdot 2\text{H}_2\text{O}$ Disordered BO_4 ; oxidation state of B atom does not balance charge or wrong number of counter-cations; $\text{C}_{10}\text{H}_8\text{S}_8$ = bis(ethylenedithio)tetrathiafulvalene Gomez-Garcia, C. J.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; LeMagueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaes, P. <i>Inorg. Chem.</i> 1995 , 4139. CSD ID: ZAXHOV.

13	<p>$\alpha\text{-K}_5[\text{B}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$ Some K counter-cations refined with partial occupancy Yamase, T.; Ishikawa, E. <i>J. Chem. Soc., Dalton Trans.</i> 1996, 1619. ICSD ID: 81833.</p>
14	<p>$\alpha\text{-K}_5[\text{BW}_{12}\text{O}_{37}(\text{H}_2\text{O})_3]\cdot 13.5\text{H}_2\text{O}$ 6 electron reduced structure Yamase, T.; Ishikawa, E. <i>J. Chem. Soc., Dalton Trans.</i> 1996, 1619. ICSD ID: 81834.</p>
15	<p>$\alpha\text{-K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 20\text{H}_2\text{O}$ Deformed Keggin (possibly wrong coord.) Yannoni, N. F. <i>Thesis, Univ. Boston</i> 1961, 1. ICSD ID: 35332.</p>
16	<p>$\alpha\text{-K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 11\text{H}_2\text{O}$ Four of the six K counter-cations were not located and therefore assumed for charge balance; some waters of hydration were refined with partial occupancy Casan-Pastor, N.; Gomez-Romero, P.; Jameson, G. B.; Baker, L. C. W. <i>J. Am. Chem. Soc.</i> 1991, 5658. ICSD ID: 71173.</p>
17	<p>$\alpha\text{-K}_{6.6}[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 7\text{H}_2\text{O}$ All W atoms, some K counter-cations, and some waters were refined with partial occupancy; supposed to be the 2 electron reduced structure, but charge does not reflect this (not enough counter-cations) Casan-Pastor, N.; Gomez-Romero, P.; Jameson, G. B.; Baker, L. C. W. <i>J. Am. Chem. Soc.</i> 1991, 5658. ICSD ID: 71174</p>
18	<p>$\alpha\text{-}[\text{C}_{10}\text{H}_8\text{S}_8]_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 2\text{C}_{10}\text{H}_8\text{S}_8\cdot 5.5\text{H}_2\text{O}$ Disordered CoO_4; $\text{C}_{10}\text{H}_8\text{S}_8$ = bis(ethylenedithio)tetrathiafulvalene Gomez-Garcia, C. J.; Ouahob, L.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; Delhaes, P. <i>Angew. Chem. Int. Ed. Engl.</i> 1994, 223. CSD ID: HAZDOB.</p>
19	<p>$\alpha\text{-}[\text{C}_{10}\text{H}_8\text{S}_8]_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 2\text{C}_{10}\text{H}_8\text{S}_8\cdot 5.5\text{H}_2\text{O}$ Disordered CoO_4; $\text{C}_{10}\text{H}_8\text{S}_8$ = bis(ethylenedithio)tetrathiafulvalene Gomez-Garcia, C. J.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; LeMagueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaes, P. <i>Inorg. Chem.</i> 1995, 4139. CSD ID: HAZDOB10.</p>
20	<p>$\alpha\text{-}[\text{C}_{10}\text{H}_8\text{S}_8]_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 2\text{C}_{10}\text{H}_8\text{S}_8\cdot 0.5\text{CH}_3\text{CN}\cdot 3\text{H}_2\text{O}$ Disordered CoO_4; $\text{C}_{10}\text{H}_8\text{S}_8$ = bis(ethylenedithio)tetrathiafulvalene Gomez-Garcia, C. J.; Gimenez-Saiz, C.; Triki, S.; Coronado, E.; LeMagueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaes, P. <i>Inorg. Chem.</i> 1995, 4139. CSD ID: ZAXHIP.</p>
21	<p>$\alpha\text{-K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]\cdot 6\text{H}_2\text{O}$ Nolan, A. L.; Allen, C. C.; Burns, R. C.; Craig, D. C.; Lawrence, G. A. <i>Australian J. Chem.</i> 2000, 59.</p>
22	<p>$\alpha\text{-K}_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 3\text{H}_2\text{O}$ Nolan, A. L.; Allen, C. C.; Burns, R. C.; Craig, D. C.; Lawrence, G. A. <i>Australian J. Chem.</i> 2000, 59.</p>
23	<p>$\alpha\text{-}[(\text{CH}_3)_4\text{N}]_6[\text{CuW}_{12}\text{O}_{40}]_{0.4}[\text{H}_2\text{W}_{12}\text{O}_{40}]_{0.6}\cdot 9\text{H}_2\text{O}$ Central position of anion is disordered with Cu(II) and two protons (0.4 Cu^{II}/0.6 2H^+) Lunk, H.-J.; Giese, S.; Fuchs, J.; Stosser, R. <i>Z. Anorg. Allg. Chem.</i> 1993, 961. CSD ID: WAKMOK.</p>

24	<p>α-[C₁₀H₈S₈]₆[CuW₁₂O₄₀]·2C₁₀H₈S₈·xH₂O</p> <p>Structure not fully determined; coord. not available; disordered CuO₄; C₁₀H₈S₈ = bis(ethylenedithio)tetrathiafulvalene Gómez-García, C. J.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Le Maguerès, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaès, P. <i>Inorg. Chem.</i> 1995, 4139. CSD ID: ZAXHAJ and ZAXHAJ01.</p>
25	<p>α-Ba₂H[Fe^{III}W₁₂O₄₀]·26H₂O</p> <p>H counter-cation assumed for charge balance; z-coordinate of O(7) assumed to be -0.079 (-0.79 in paper) Weiner, H.; Lunk, H. J.; Fuchs, J.; Ziemer, B.; Stoesser, R.; Pietzsch, C.; Reich, P. <i>Zeitschrift fuer Anorganische und Allgemeine Chemie</i> 1991, 191. ICSD ID: 33857.</p>
26	<p>α-[[(CH₃)₅Cp]₂Fe^{III}]₄[HFe^{III}W₁₂O₄₀]·CH₃CN·3H₂O</p> <p>H atom associated with POM assumed for charge balance Le Maguerès, P.; Ouahab, L.; Golhen, S.; Grandjean, D.; Peña, O.; Jegaden, J.-C.; Gómez-García, C. J.; Delhaès, P. <i>Inorg. Chem.</i> 1994, 5180. CSD ID: YEMTAL.</p>
27	<p>α-[C₁₀H₈S₈]₆[Fe^{III}W₁₂O₄₀]·2C₁₀H₈S₈·9H₂O</p> <p>Disordered FeO₄; oxidation state of Fe atom does not agree with charge balance; C₁₀H₈S₈ = bis(ethylenedithio)tetrathiafulvalene Gómez-García, C. J.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Le Maguerès, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaès, P. <i>Inorg. Chem.</i> 1995, 4139. CSD ID: ZAXHEL.</p>
28	<p>α-[(CH₃)₄N]₅[GaMo₂W₁₀O₄₀]</p> <p>Coord. not available Tkach, V. I.; Taiganok, L. P. <i>Koord. Khim.</i> 1982, 943. CSD ID: BOSCIIV.</p>
29	<p>α-[(CH₃)₄N]₇[GaMo₂W₁₀O₄₀]</p> <p>Coord. not available; number of cations does not agree with charge balance or possibly mixed oxidation state of Mo and/or W atoms Tkach, V. I.; Taiganok, L. P. <i>Koord. Khim.</i> 1982, 943. CSD ID: BOSCOB.</p>
30	<p>α-[(CH₃)₄N]₅[Ga^{III}MoW₁₁O₄₀]</p> <p>Coord. not available Tkach, V. I.; Taiganok, L. P. <i>Koord. Khim.</i> 1982, 943. CSD ID: BOSCAN.</p>
31	<p>α-[(CH₃)₄N]₆[Ga^{III}MoW₁₁O₄₀]</p> <p>Coord. not available; number of cations does not agree with charge balance or possibly mixed oxidation state of Mo and/or W atoms Tkach, V. I.; Taiganok, L. P. <i>Koord. Khim.</i> 1982, 943. CSD ID: BOSKER.</p>
32	<p>α-K₇[Ga^{III}Pb^{II}W₁₁O₃₉]·16H₂O</p> <p>No terminal ligand (oxo or aqua) on Pb Tourne, G. F.; Tourne, C. M.; Schouten, A. <i>Acta Cryst. B</i> 1982, 1414. ICSD ID: 27239.</p>
33	<p>α-K₃H₂[Ge^{IV}V^VMo₃W₈O₄₀]·4H₂O</p> <p>12 metal sites disordered (0.667 W/0.250 Mo/0.083 V) Wu, Q.-Y.; Wnag, X.-F.; Song, Y.-L. <i>Gaodeng Xuexiao Huaxue Xuebao</i> 1998, 934. ICSD ID: 87548.</p>
34	<p>α-K₃H[H₃Ge^{IV}V^VW₉O₄₀]·11H₂O</p> <p>H counter-cation and H atoms associated with POM assumed for charge balance Chen, Y.-G.; Qu, L. Y.; Peng, J.; Yu, M. <i>Chemical Research in Chinese Universities</i> 1993, 6. ICSD ID: 74026.</p>

35	<p>$\alpha\text{-}[(4\text{-CH}_3)\text{Py}]_5[\text{H}_4\text{Ge}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot\text{CH}_3\text{CN}$ H atoms assumed for unknown reason Nui, J.; Wang, J.; Song, L.; Zhou, Z. <i>Chinese J. Inorg. Chem.</i> 1998, 303. CSD ID: MAVQIJ.</p>
36	<p>$\alpha\text{-}[\text{C}_{14}\text{H}_8\text{S}_4]_4[\text{HGe}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 2\text{C}_{14}\text{H}_8\text{S}_4\cdot 4\text{H}_2\text{O}$ H atom assumed for charge balance; $\text{C}_{14}\text{H}_8\text{S}_4$ = dibenzotetrathiafulvalene Chen, Y.-G.; Liu, J.-F.; Xing, Y.; Lin, Y.-H.; Jia, H.-Q. <i>Chinese J. Struct. Chem.</i> 1998, 105. CSD ID: PIHQAY.</p>
37	<p>$\alpha\text{-Cs}_3\text{H}_3[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$ Coord. not available; H counter-cations assumed for charge balance Santos, J. A. <i>Proc. Royal Soc. London, Ser. A: Math. and Phys. Sci.</i> 1935, 309. ICSD ID: 33117.</p>
38	<p>$\alpha\text{-Rb}_4\text{H}_8[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot 18\text{H}_2\text{O}$ Number of H counter-cations seems high (probably should be only 2); 12 W metal sites disordered over 2 positions (0.333/0.667); all Rb counter-cations refined with partial occupancy; H counter-cations assumed for charge balance Jeannin, Y.; Launay, J. P.; Sedjadi, S. M. A. <i>Inorg. Chem.</i> 1980, 2933. ICSD ID: 16468.</p>
39	<p>$\alpha\text{-}[(\text{CH}_3)_4\text{N}]_6[\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$ Asami, M.; Ichida, H.; Sasaki, Y. <i>Acta Cryst. C</i> 1984, 35. ICSD ID: 41163.</p>
40	<p>$\alpha\text{-Cs}_5[\text{PCo}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 3\text{H}_2\text{O}$ Disordered PO_4; Co disordered over 12 positions (0.083 Co/0.917 W); several O atoms refined with partial occupancy; aqua ligand on Co assumed for charge balance Klevtsova, R. F.; Yurchenko, E. N.; Glinskaya, L. A.; Kuznetsova, L. I.; Detusheva, L. G.; Lazarenko, T. P. <i>Zhurnal. Strukturnoi. Khimii.</i> 1991, 102. ICSD ID: 39500</p>
41	<p>$\alpha\text{-K}_6\text{Na}_1[\text{PCu}^{\text{II}}_2(\text{OH}_2)_2\text{W}_{10}\text{O}_{38}]\cdot 13\text{H}_2\text{O}$ Cu atoms disordered over 12 positions (0.195 Cu/0.805 W); addenda atoms rounded to integers (actually $\text{Cu}_{2.3}\text{W}_{9.7}$); aqua ligands on Cu atoms assumed for charge balance Gomez-Garcia, C. J.; Coronado, E.; Gomez-Romero, P.; Casan-Pastor, N. <i>Inorg. Chem.</i> 1993, 89. ICSD ID: 72475.</p>
42	<p>$\alpha\text{-}[(\text{CH}_3)_5\text{Cp}]_4[\text{Fe}^{\text{III}}]_4[\text{HPCu}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 6\text{CH}_3\text{CN}$ Disordered PO_4; Cu disordered over 6 positions (4 at 0.05 Cu/0.95 W and 2 at 0.2 Cu/0.8 W); Cu refinements do not equal full occupancy; H atom and terminal aqua ligand assumed for charge balance Golhen, S.; Ouahab, L.; Grandjean, D.; Molinie, P. <i>Inorg. Chem.</i> 1998, 1499. CSD ID: NOCLIA.</p>
43	<p>$\alpha\text{-H}_3[\text{PMo}_6\text{W}_6\text{O}_{40}]\cdot 3(\text{CH}_3)_2\text{O}$ Mo atoms disordered over 12 positions (0.5 Mo/0.5 W); terminal O(7) deformed (possibly wrong coord.); H counter-cations assumed for charge balance Peng, J.; Zhan, Y.; Wang, E.; Xing, Y.; Jia, H. Q. <i>J. Mol. Struct.</i> 1998, 213. CSD ID: BEYGER.</p>
44	<p>$\alpha\text{-}[\text{NH}_3(\text{CH}_2)_6\text{NH}_3]_3[\text{PMo}_4\text{W}_8\text{O}_{40}]$ Disordered PO_4; Mo atoms disordered over 12 positions (2 at 0.233 Mo/0.767 W, 4 at 0.415 Mo/0.585, 4 at 0.430 Mo/0.570 W, and 2 at 0.346 Mo/0.654 W); mixed oxidation states for W and Mo (V/VI); Mo/W refinements actually equal 4.5/7.5 ratio (4/8 ratio assumed by rounding); one cation is disordered Gabriel, J.-C. P.; Nagarajan, R.; Natarajan, S.; Cheetham, A. K.; Rao, C. N. R. <i>J. Solid State Chem.</i> 1997, 257. CSD ID: NATNAX.</p>

45	<p>β-[(CH₃)₄N]₃[PMo₃W₉O₄₀] Mo atoms all located in Site I positions (each in different non-rotated triad; opposite side of POM from rotated triad) Kawafune, I.; Matsubayashi, G. <i>Chem. Lett.</i> 1992, 1869. CSD ID: HADTOV.</p>
46	<p>α-[(C₄H₉)₄N]₃[PMo₃W₉O₄₀] Coord. not available Kawafune, I.; Matsubayashi, G. <i>Bull. Chem. Soc. Japan</i> 1994, 694. CSD ID: ZEFJUP.</p>
47	<p>α-K₆[PMo₃W₉O₄₀]$\cdot$13H₂O Three Mo disordered over 12 positions (0.25 Mo/0.75 W) Leclaire, A.; Borel, M. M.; Chardon, J.; Raveau, B. <i>Materials Research Bulletin</i> 1995, 1075. ICSD ID: 80443.</p>
48	<p>β-Cs₆[P(NbO₂)₃W₉O₃₇]$\cdot$HCl$\cdot$6.5H₂O Terminal ligands on Nb atoms are η^2-peroxides; some of the Cs, Nb, peroxide oxygen, and waters were refined with partial occupancy Harrup, M. K.; Kim, G.-S.; Zeng, H.; Johnson, R. P.; VanDerveer, D.; Hill, C. L. <i>Inorg. Chem.</i> 1998, 5550. ICSD ID: 85791.</p>
49	<p>α-[(C₄H₉)₄N]₃[PNb^VW₁₁O₄₀(Ge^I(CH₃)₃)]$\cdot$Et₂O Trimethyl germanyl is disordered over two positions (occupancies of 0.54 and 0.46) Radkov, E. V.; Beer, R. H. <i>Inorg. Chim. Acta</i> 2000, 297, 191. CSD ID: QIMWAK.</p>
50	<p>α-K₆Na[PNi^{II}(OH₂)₃W₉O₃₇(WO₂)(OH₂)]$\cdot$12H₂O German version; aqua ligands on Ni atoms assumed for charge balance Gomez-Garcia, C. J.; Coronado, E.; Ouahab, L. <i>Angew. Chem.</i> 1992, 660. ICSD ID: 71901.</p>
51	<p>α-Cs₂[H₂PNi₃(OH)₃(OH₂)₃W₉O₃₄(Ni(OH₂)₃)]$\cdot$5H₂O Kortz, U.; Teze, A.; Herve, G. <i>Inorg. Chem.</i> 1999, 2038.</p>
52	<p>α-Cs₅[PNi^{II}(OH₂)W₁₁O₃₉]$\cdot$2H₂O Disordered PO₄; Ni disordered over 12 positions (0.083 Ni/0.917 W); aqua ligand on Ni assumed for charge balance; all Cs counter-cations refined with partial occupancy Weakley, T. J. R. <i>J. Crystallographic & Spectroscopic Research</i> 1987, 383. ICSD ID: 68064.</p>
53	<p>α-Cs₅[PNi^{III}(OH₂)W₁₁O₃₉]$\cdot$2H₂O Disordered PO₄; Ni disordered over 12 positions (2 at 0.041 Ni/0.786 W, 10 at 0.041 Ni/0.393 W); aqua ligand on Ni assumed for charge balance; all Cs counter-cations and several O atoms refined with partial occupancy Weakley, T. J. R. <i>J. Crystallographic & Spectroscopic Research</i> 1987, 383. ICSD ID: 68065.</p>
54	<p>α-[C₁₀H₈S₈]₅[PNi^{II}(OH₂)W₁₁O₃₉]$\cdot$3C₁₀H₈S₈$\cdot$2H₂O Disordered PO₄; Ni atoms disordered over 2 positions (0.5 Ni/0.5 W); terminal aqua ligand on Ni assumed for charge balance; C₁₀H₈S₈ = bis(ethylenedithio)tetrathiafulvalene; Cambridge database incorrectly lists POM as PNi₂W₁₀ with two H atoms associated with POM Coronado, E.; Galan-Mascaros, J. R.; Gimenez-Saiz, C.; Gomez-Garcia, C. J.; Triki, S. <i>J. Am. Chem. Soc.</i> 1998, 4671. CSD ID: SEYQES.</p>

55	<p>$\alpha\text{-}[(\text{Et})_2\text{NH}_2]_4\text{Na}[\text{H}_2\text{PTi}^{\text{II}}_2(\text{OH}_2)_2\text{W}_{10}\text{O}_{38}]\cdot 11\text{H}_2\text{O}$ Ti atoms disordered over two positions (one at 0.720 Ti/0.280 W and one at 0.698 Ti/0.302 W); H atoms associated with POM and terminal aqua ligands on Ti atoms assumed for charge balance; occupancy refinements of Ti atoms do not total two full atoms Ozeki, T.; Yamase, T. <i>Acta Cryst., C</i> 1991, 693. CSD ID: SITZIE.</p>
56	<p>$\alpha\text{-}[(\text{CH}_3)_2\text{CHNH}_3]_6\text{H}[\text{PTi}^{\text{II}}_2(\text{O}_2)_2\text{W}_{10}\text{O}_{38}]\cdot \text{H}_2\text{O}$ Ti atoms disordered over 12 metal sites (0.16 Ti/0.84 W) Yamase, T.; Ozeki, T.; Motomura, S. <i>Bull. Chem. Soc. Japan</i> 1992, 1453. CSD ID: YAGCEO.</p>
57	<p>$\alpha\text{-}[(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_5[\text{PTi}^{\text{II}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]\cdot 4\text{H}_2\text{O}$ Ti atom disordered over 12 metal sites (0.08 Ti/0.92 W); one cation is disordered; terminal aqua ligands on Ti atoms assumed for charge balance Yamase, T.; Ozeki, T.; Motomura, S. <i>Bull. Chem. Soc. Japan</i> 1992, 1453. CSD ID: YAGBUD.</p>
58	<p>$\alpha\text{-}[(\text{CH}_3)_2\text{CH}_2\text{NH}_2]_5[\text{PTi}^{\text{II}}(\text{O}_2)\text{W}_{11}\text{O}_{39}]\cdot 4\text{H}_2\text{O}$ Ti atom disordered over 12 metal sites (0.08 Ti/0.92 W); one cation is disordered Yamase, T.; Ozeki, T.; Motomura, S. <i>Bull. Chem. Soc. Japan</i> 1992, 1453. CSD ID: YAGCAK.</p>
59	<p>$\beta\text{-Cs}_{5.4}\text{H}_{0.6}[\text{PV}_3\text{W}_9\text{O}_{40}]$ Kawafune, I.; Tamura, H.; Matsubayashi, G. <i>Bull. Chem. Soc. Japan</i> 1997, 2455.</p>
60	<p>$\gamma\text{-Cs}_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]\cdot 6.5\text{H}_2\text{O}$ Some Cs counter-cations refined with partial occupancy Domaille, P. J.; Harlow, R. L. <i>J. Am. Chem. Soc.</i> 1986, 2108. ICSD ID: 63172.</p>
61	<p>$\alpha\text{-}[\text{NH}_4]_4\text{H}[\text{PV}_2\text{W}_{10}\text{O}_{40}]\cdot 2.5\text{H}_2\text{O}$ V atoms are disordered over 12 positions with variable occupancies (avg. = 0.167) You, W.-S.; Wang, Y.-B.; Wang, E.; Luan, G.-Y.; Han, Z.-B. <i>Fenzi Kexue Xuebao</i> 2000, 77.</p>
62	<p>$\alpha\text{-H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 30\text{H}_2\text{O}$ Coord. not available; H counter-cations assumed for charge balance Keggin, J. F. <i>Nature</i> 1933, 351. ICSD ID: 38907.</p>
63	<p>$\alpha\text{-H}_3[\text{PW}_{12}\text{O}_{40}]$ H counter-cations assumed for charge balance; coord. of O(1) probably wrong Keggin, J. F. <i>Proc. of the Royal Soc. Of London, Ser. A: Mathematical and Physical Sciences</i> 1934, 75. ICSD ID: 31897.</p>
64	<p>$\alpha\text{-Cs}_3[\text{PW}_{12}\text{O}_{40}]\cdot \text{H}_2\text{O}$ Coord. not available Santos, J. A. <i>Proc. Royal Soc. London, Ser. A: Math. and Phys. Sci.</i> 1935, 309. ICSD ID: 33115.</p>
65	<p>$\alpha\text{-H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 29\text{H}_2\text{O}$ H counter-cations assumed for charge balance; wrong coord. in database Bradley, J. A.; Illingworth, J. W. <i>Proc. of the Royal Soc. Of London, Ser. A: Mathematical and Physical Sciences</i> 1936, 113. ICSD ID: 36274.</p>
66	<p>$\alpha\text{-H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 29\text{H}_2\text{O}$ Coord. not available; H counter-cations assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936, 256. ICSD ID: 38540.</p>

67	α-H₃[PW₁₂O₄₀]·24H₂O Coord. not available; H counter-cations assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38541.
68	α-H₃[PW₁₂O₄₀]·14H₂O Coord. not available; H counter-cations assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1939 , 394. ICSD ID: 38590.
69	α-NaH₂[PW₁₂O₄₀]·12H₂O Deformed at terminal O(9) (possibly wrong coord.); H counter-cations assumed for charge balance Allmann, R.; d'Amour, H. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1975 , 161. ICSD ID: 4159.
70	α-(H₅O₂)₃[PW₁₂O₄₀] H ₅ O ₂ = aquaoxonium Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. <i>Acta. Cryst. B</i> 1977 , 1038. ICSD ID: 904 and 908.
71	α-H₃[PW₁₂O₄₀]·21H₂O H counter-cations assumed for charge balance Spirlett, M. R.; Busing, W. R. <i>Acta. Cryst. B</i> 1978 , 907. ICSD ID: 1534.
72	α-[(C₄H₉)₄N]₃[PW₁₂O₄₀] Coord. not available Fuchs, J.; Thiele, A.; Palm, R. <i>Angew. Chem., Int. Ed. Engl.</i> 1982 , 789. CSD ID: BIZMOM.
73	γ-[(C₄H₉)₄N]₃[PW₁₂O₄₀] Coord. not available Fuchs, J.; Thiele, A.; Palm, R. <i>Angew. Chem., Int. Ed. Engl.</i> 1982 , 789. CSD ID: BIZMUS.
74	γ-[(C₄H₉)₄N]₃[PW₁₂O₄₀] Coord. not available; disordered structure Fuchs, J.; Thiele, A.; Palm, R. <i>Z. Naturforsch., Teil B</i> 1982 , 1418. CSD ID: BIZMUS10.
75	α-[C₆H₄S₄][(Et)₄N]₂[PW₁₂O₄₀]·5C₆H₄S₄ Coord. not available; C ₆ H ₄ S ₄ = tetrathiafulvalene Ouahab, L.; Bencharif, M.; Grandjean, D.; <i>C. R. Seances Acad. Sci., Sec. 2</i> 1988 , 749. CSD ID: VEGGOD.
76	α-[C₁₀H₂₅N₄O₂]₃[PW₁₂O₄₀] C ₁₀ H ₂₅ N ₄ O ₂ = hydrogen-bis(1,1,3,3-tetramethylurea) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. <i>J. Am. Chem. Soc.</i> 1988 , 5471. CSD ID: GICDAX.
77	α-[C₁₀H₂₁N₄O₂]₃[PW₁₂O₄₀] Coord. not available; disordered anion; C ₁₀ H ₂₁ N ₄ O ₂ = hydrogen-bis(1,3-dimethyl-2-imidizolidinone) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. <i>J. Am. Chem. Soc.</i> 1988 , 5471. CSD ID: GICDEB.
78	α-[C₉H₈NO]₃[PW₁₂O₄₀]·4EtOH·2H₂O Disordered PO ₄ ; two terminal oxos disordered as well as one cation and two water molecules; C ₉ H ₈ NO = 8-hydroxyquinolinium Attanasio, D.; Bonamico, M.; Fares, V.; Imperatori, P.; Suber, L. <i>J. Chem. Soc., Dalton Trans.</i> 1990 , 3221. CSD ID: SIJLEC.

79	α-[(CH₃)₂NH₂]₃[PW₁₂O₄₀]·2H₂O Deformed at terminal O(21) and O(21a) (possibly wrong coord.) Jianping, D.; Yidong, G.; Guang, W.; Boyi, W. <i>Chinese J. Inorg. Chem.</i> 1991 , 1. CSD ID: YADFIS.
80	α-[C₁₀H₁₂Se₄]₃[PW₁₂O₄₀] Disordered PO ₄ ; C ₁₀ H ₁₂ Se ₄ = 3,3_,4,4_-tetramethyl-2,2_,5,5_- tetraselenafulvalene Ouahab, L.; Grandjean, D.; Bencharif, M. <i>Acta Cryst., C</i> 1991 , 2670. CSD ID: VOGHOO.
81	α-[C₆H₄S₄][(Et)₄N]₂[PW₁₂O₄₀]·5C₆H₄S₄ Disordered PO ₄ ; tetraethylammonium cation disordered; C ₆ H ₄ S ₄ = tetrathiafulvalene Ouahab, L.; Bencharif, M.; Mhanni, A.; Pelloquin, D.; Halet, J.-F.; Pena, O.; Padiou, J.; Grandjean, D.; Garrigou-Lagrange, C.; Amiell, J.; Delhaes, P. <i>Chem Mat.</i> 1992 , 666. CSD ID: VEGGOD10.
82	α-[C₅H₆N]₃[PW₁₂O₄₀]·3C₅H₅N Disordered PO ₄ Hashimoto, M.; Misuno, M. <i>Acta Cryst., C</i> 1994 , 231. CSD ID: HATVON.
83	α-[C₅H₆N]₅[PW₁₂O₄₀] Disordered PO ₄ ; one pyridinium cation is equally disordered over two positions; charge does not agree for usual fully oxidized Keggin (possibly W ^V /W ^{VI} mixture or wrong number of cations) Tolkacheva, E. O.; Sergienko, V. S.; Ilyukhin, A. B.; Minin, V. V. <i>Zh. Neorg.</i> <i>Chim.</i> 1996 , 1791. CSD ID: REBRAR.
84	α-[C₆H₁₄N₂]₂[PW₁₂O₄₀] Coord. not available; anion charge does not agree with usual fully oxidized POM; [C ₆ H ₁₄ N ₂] ²⁺ = 1,4-diazoniabicyclo(2.2.2)octane Holscher, U.; Gammersbach, A.; Zibrowius, B.; Englert, U.; Holderich, W. F. <i>Chem. Ind. (Dekker)</i> 1997 , 345. CSD ID: NUQPIY.
85	α-H₃[PW₁₂O₄₀]·6 C₁₄H₂₀O₅·13H₂O Disordered PO ₄ ; some disordered waters; H counter-cations assumed for charge balance; C ₁₄ H ₂₀ O ₅ = benzo-15-crown-5 You, W.; Wang, E.; Zhang, H.; Xu, L.; Wang, Y. <i>J. Mol. Struct.</i> 2000 , 554, 141. CSD ID: SUXRAE.
86	α-[Ni^{II}(2,2'-bpy)₃]_{1.5}[PW^V₂W^{VI}₁₀O₄₀(Ni^{II}(2,2'-bpy)₂(OH₂))]₁·0.5H₂O Xu, Y.; Zhang, K.-L.; Zhang, Y.; You, X.-Z.; Xu, J.-Q. <i>Chem. Commun.</i> 2000 , 153. CSD ID: WIXSIF.
87	α-[NH₃(CH₂)₂NH₂]₃[PW₁₂O₄₀]·11H₂O Luan, G.-Y.; Wang, M.-H.; Wang, E.; Han, Z.-B.; You, W.-S. <i>Fenzi Kexue</i> <i>Xuebao</i> 2000 , 211.
88	α-[Cu₃(4,4'-bipy)₅(CH₃CN)₂][PW₁₂O₄₀]·2C₆H₅CN Inman, C.; Knaust, J. M.; Keller, S. W. <i>Chem. Commun.</i> 2002 , 156.
89	α-[(C₄H₉)₄N]₃[H₂SiAs^{III}W₁₁O₃₉] As atom disordered over 12 positions (0.08 As/O.92 W); H atoms assumed for charge balance Ji, S.-J.; Yu, H.; Lang, J.-P.; Cai, J.-H.; Kang, B.-S.; Xin, X.-Q. <i>Chinese J.</i> <i>Struct. Chem.</i> 1997 , 290.

90	<p>α-K₃H₄[SiCr₃(OH)₂W₉O₃₇]$\cdot$11H₂O Position of aqua ligand on Cr(1) not well-defined; H counter-cations and terminal aqua ligands on Cr atoms assumed for charge balance Wassermann, K.; Lunk, H.-J.; Palm, R.; Fuchs, J. <i>Acta. Cryst. C</i> 1994, 348. ICSD ID: 74524.</p>
91	<p>α-K₅H[SiMnMo₂W₉O₄₀]$\cdot$11H₂O 12 metal atoms (Mn, Mo, and W) disordered over metal sites in random distribution Zhu, Z.; Chen, Y.; Zhou, D.; Liu, J.; Liu, Z.; Xie, H. <i>J. Mol. Struct.</i> 2001, 103.</p>
92	<p>γ-[PhN(CH₃)₃]₄[SiMn^{III}₂(OH)₂(OH₂)₂W₁₀O₃₇]$\cdot$2CH₃CN$\cdot$H₂O Terminal aqua ligands and μ-hydroxos on Mn atoms assumed for charge balance and confirmed by bond valence sum calculations Zhang, X.-Y.; O'Connor, C. J.; Jameson, G. B.; Pope, M. T. <i>Inorg. Chem.</i> 1996, 30. CSD ID: ZOPRUR.</p>
93	<p>α-[C(NH₂)₃]₆[SiMn^{II}(OH)₂W₁₁O₃₉]$\cdot$2.5H₂O Mn disordered over 12 positions (0.083 Mn/0.917 W); missing terminal oxo at X(5) (arbitrary metal site labelling due to disorder); terminal aqua ligand on Mn assumed for charge balance; some waters refined with partial occupancy Sergienko, V. S.; Porai-Koshito, M. A. <i>Zh. Neorg. Khim.</i> 1985, 2282. CSD ID: DISNIC and ICSD ID: 61432.</p>
94	<p>γ-Cs₃[(Et)₄N][SiMo₂S₂W₁₀O₃₈]$\cdot$6H₂O Edge-sharing S atoms bridge the Mo atoms to each other Cadot, E.; Bereau, V.; Marg, B.; Halut, S.; Secheresse, F. <i>Inorg. Chem.</i> 1996, 3099. CSD ID: TAVRAJ.</p>
95	<p>β-K₄[SiMoW₁₁O₄₀]$\cdot$9H₂O Mo disordered over 3 site I-type positions (2 at 0.25 Mo/0.75 W and 1 at 0.5 Mo/0.5 W); z-coordinate of Si(1) published at 0.6989 which is wrong (actually 0.5989) Robert, F.; Tezé, A.; Hervé, G.; Jeanin, Y. <i>Acta Cryst. B</i> 1980, 11. ICSD ID: 10507.</p>
96	<p>α-K₈[SiNb^V₄W₈O₄₀]$\cdot$12H₂O Nb atoms disordered over 12 positions (0.333 Nb/0.667 W); some of the oxygen and potassium atoms refined with partial occupancy Yue, B.; Tang, L.-H.; Rui, C.-G.; Liu, H.-Z.; Jin, S.-L.; Zhu, S.-S.; Liu, J.; Chen, M.-Q. <i>Chemical Research in Chinese Universities</i> 1997, 195. ICSD ID: 83813.</p>
97	<p>α-Cs₆H[SiNb₃W₉O₄₀]$\cdot$4H₂O Kim, G.-S.; Zeng, H.; Rhule, J. T.; Weinstock, I. A.; Hill, C. L. <i>Chem. Commun.</i> 1999, 1651.</p>
98	<p>α-K₄H₃[SiNb₃W₉O₄₀]$\cdot$4H₂O Liu, J.; Pan, X.-K.; Mei, W.-J.; Ji, L.-N. <i>Zhongshan Daxue Xuebao, Ziran Kexueban</i> 2001, 81.</p>
99	<p>α-Cs₆[SiRh^{II}(CH₂COOH)W₁₁O₃₉]$\cdot$6H₂O Carboxy group is disordered over 2 sites (occupancy of 0.6/0.4); carboxy group assumed to be protonated for charge balance Wei, X.; Dickman, M. H.; Pope, M. T. <i>J. Am. Chem. Soc.</i> 1998, 10254. CSD ID: SIRNOW.</p>
100	<p>β-Cs₄H₃[Si(Sn^{III}Ph)₃W₉O₃₇]$\cdot$8H₂O Ph rings slightly twisted; H counter-cations assumed for charge balance Xin, F.; Pope, M. T.; Long, G. J.; Rosso, U. <i>Inorg Chem.</i> 1996, 1207. CSD ID: ZUBKEM.</p>

101	α-Be₂[SiW₁₂O₄₀]$\cdot$31H₂O Coord. not available.; H counter-cation assumed for charge balance Hoard, J. L. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1933 , 217. ICSD ID: 38510.
102	α-H₄[SiW₁₂O₄₀]$\cdot$24H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1935 , 402. ICSD ID: 38518.
103	α-Fe^{III}H[SiW₁₂O₄₀]$\cdot$28H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 379. ICSD ID: 38521.
104	α-Fe^{III}H[SiW₁₂O₄₀]$\cdot$24H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 379. ICSD ID: 38522.
105	α-Fe^{III}H[SiW₁₂O₄₀]$\cdot$30H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 379. ICSD ID: 38523.
106	α-Cr^{III}H[SiW₁₂O₄₀]$\cdot$28H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 379. ICSD ID: 38524.
107	α-Cr^{III}H[SiW₁₂O₄₀]$\cdot$24H₂O Coord. not available.; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 379. ICSD ID: 38525.
108	α-Th^{IV}[SiW₁₂O₄₀]$\cdot$27H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38530.
109	α-Th^{IV}[SiW₁₂O₄₀]$\cdot$30H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38531.
110	α-Ca₂[SiW₁₂O₄₀]$\cdot$26H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38532.
111	α-Ba₂[SiW₁₂O₄₀]$\cdot$24H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38533.
112	α-Zn₂[SiW₁₂O₄₀]$\cdot$27H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38534.

113	α-Cu₂[SiW₁₂O₄₀]·27H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38535.
114	α-Li₃H[SiW₁₂O₄₀]·26H₂O Coord. not available; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38536.
115	α-Li₃H[SiW₁₂O₄₀]·24H₂O Coord. not available; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38537.
116	α-K₄[SiW₁₂O₄₀]·18H₂O Coord. not available Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1936 , 256. ICSD ID: 38538.
117	α-Fe^{III}H[SiW₁₂O₄₀]·20H₂O Coord. not available; H counter-cation assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1937 , 304. ICSD ID: 38555.
118	α-H₄[SiW₁₂O₄₀]·14H₂O Coord. not available.; H counter-cations assumed for charge balance Kraus, O. <i>Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie</i> 1939 , 394. ICSD ID: 38587.
119	β-K₄[SiW₁₂O₄₀]·9H₂O Coord. not available Yamamura, K.; Sasaki, Y. <i>J. Chem. Soc. Chem. Commun.</i> 1973 , 648.
120	α-Ba₂[SiW₁₂O₄₀]·12H₂O Kobayashi, A.; Sasaki, Y. <i>Bull. Chem. Soc. Japan</i> 1975 , 885. ICSD ID: 4161.
121	β-K₄[SiW₁₂O₄₀]·9H₂O Matsumoto, K. Y.; Kobayashi, A.; Sasaki, Y. <i>Bull. Chem. Soc. Japan</i> 1975 , 3146. ICSD ID: 4160.
122	α-[(CH₃)₄N]₄[SiW₁₂O₄₀] Fuchs, J.; Thiele, A.; Palm, R. <i>Z. Naturforsch., Teil B</i> 1981 , 161. CSD ID: MAWSIA.
123	β-[(C₄H₉)₄N]₄[SiW₁₂O₄₀] Fuchs, J.; Thiele, A.; Palm, R. <i>Z. Naturforsch., Teil B</i> 1981 , 161. CSD ID: MAWSIB.
124	α-[C₁₀H₈S₈]₄[SiW₁₂O₄₀]·4C₁₀H₈S₈ Disordered counter-cation; C ₁₀ H ₈ S ₈ = bis(ethylenedithio)tetrathiafulvalenium Davidson, A.; Boubekur, K.; Penicaud, A.; Auban, P.; Lenoir, C.; Batail, P.; Herve, G. <i>Chem. Commun.</i> 1989 , 1373. CSD ID: JAPWIG.
125	α-H₄[SiW₁₂O₄₀]·8(CH₃)₂SO Hydrogen counter-cations assumed for charge balance; disordered dimethylsulfoxide solvate Oniani, E. S.; Sergienko, V. S.; Chuvaev, V. F.; Mistryukov, A. E. <i>Zh. Neorg. Khim.</i> 1991 , 2048. CSD ID: KUPKAH.

126	<p>α-[C₆H₄S₄]₂[(Et)₄N]H[SiW₁₂O₄₀]$\cdot$4C₆H₄S₄ Disordered SiO₄; H counter-cation assumed for charge balance; C₆H₄S₄ = tetrathiafulvalene Ouahab, L.; Bencharif, M.; Mhanni, A.; Pelloquin, D.; Halet, J.-F.; Pena, O.; Padiou, J.; Grandjean, D.; Garrigou-Lagrange, C.; Amiell, J.; Delhaes, P. <i>Chem Mat.</i> 1992, 666. CSD ID: PAKREY.</p>
127	<p>α-H₄[SiW₁₂O₄₀]$\cdot$4C₆H₁₈N₃OP$\cdot$2H₂O H counter-cations assumed for charge balance; C₆H₁₈N₃OP = hexamethylphosphoramidate Niu, J.-Y.; You, X.-Z.; Duan, C.-Y.; Fun, H.-K.; Zhou, Z.-Y. <i>Inorg. Chem.</i> 1996, 4211. CSD ID: TEZLIT.</p>
128	<p>γ-Cs₅[(Et)₄N][SiW₁₂S₂O₃₈]$\cdot$7H₂O Edge-sharing S atoms replace two O atoms Cadot, E.; Bereau, V.; Marg, B.; Halut, S.; Secheresse, F. <i>Inorg. Chem.</i> 1996, 3099. CSD ID: TAVQUC.</p>
129	<p>α-[C₈H₁₃N₂]₄[SiW₁₂O₄₀]$\cdot$2(CH₃)₂NCHO Disordered SiO₄; C₈H₁₃N₂ = 4-dimethylamino-1-methylpyridylammonium Zhang, X.-M.; Shan, B.-Z.; You, X.-Z.; Zhou, Z.-Y.; Zhou, X.-G. <i>Polyhedron</i> 1997, 713. CSD ID: RIGSAB.</p>
130	<p>α-[C₁₀H₈S₆]₄[SiW₁₂O₄₀]$\cdot$CH₃CN No coord. available; structure not fully determined; two cation molecules disordered; C₁₀H₈S₆ = bis(ethylenedithio)tetrathiafulvalene Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J.; Rovira, C.; Tarrés, J.; Triki, S. Veciana, J. <i>J. Mater. Chem.</i> 1998, 313. CSD ID: PUQCUZ.</p>
131	<p>α-[C₁₄H₈S₄]₃H[SiW₁₂O₄₀]$\cdot$3C₁₄H₈S₄$\cdot$2H₂O Coord. not available; H counter-cation assumed for charge balance; C₁₄H₈S₄ = dibenzotetrathiafulvalene Yaguang, C.; Zhiping, Z.; Jingfu, L.; Yonghua, L.; Yan, X.; Hengqing, J. <i>Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)</i> 1998, 281. CSD ID: LOJWOW.</p>
132	<p>α-[C₈H₂₆Np^{VI}O₇S₄]₄[SiW₁₂O₄₀] Disordered SiO₄; S(1) from dimethylsulfoxide group disordered over two positions (0.75/0.25); C₈H₂₆NpO₇S₄ = aqua-tetrakis(dimethylsulfoxide-O)-dioxo-neptunium(VI) Charushnikova, I. A.; Starikova, Z. A.; Fedoseev, A. M.; Budantseva, N. A. <i>Zh. Neorg. Khim.</i> 2000, 1978. CSD ID: QEVNIO.</p>
133	<p>α-[Na(OH₂)₂]₂[VO(OH₂)₅][SiW₁₂O₄₀]$\cdot$4H₂O Teze, A.; Marchal-Roch, C.; So, H.; Fournier, M.; Herve, G. <i>Solid State Sciences</i> 2001, 329.</p>
134	<p>γ-[(C₄H₉)₄N]₄[SiW₁₂O₄₀] Missing last two C atoms on TBA cations Tézé, A.; Cadot, E.; Béreau, V.; Hervé, G. <i>Inorg. Chem.</i> 2001, 2000. CSD ID: QOLPIQ.</p>
135	<p>α-[NH₃(CH₂)₂NH₃]₂[V^VV^VW₁₁O₄₀]$\cdot$6H₂O One V atom (addenda position) is disordered over 12 positions (0.08 V/0.92 W) Glinskaya, L. A.; Yurchenko, E. N.; Klevtsova, R. F.; Derkach, L. V.; Rios, A. M.; Lazarenko, T. P. <i>Zh. Strukt. Khim.</i> 1989, 82. CSD ID: JEMVUS.</p>

136	<p>α-[(CH₃)₂NHCHO]₄[V^VV^VW₁₁O₄₀]·2(CH₃)₂NCHO·2H₂O Disordered VO₄; one V atom (addenda position) is disordered over 12 positions (0.08 V/0.92 W) Klevtsova, R. F.; Glinskaya, L. A.; Yurchenko, E. N.; Dekach, L. V.; Rios, A. M.; Lazarenko, T. P. <i>Zh. Strukt. Khim.</i> 1990, 117. CSD ID: JINNEZ.</p>
137	<p>α-K₇[V^VV^VW₈O₄₀]·12H₂O 4 V atoms disordered over 12 metal sites (0.333 V/0.667 W); coord. Of O(2) probably wrong Nichifawa, K.; Kobayashi, A.; Sasaki, Y. <i>Bull. Chem. Soc. Japan</i> 1975, 3152. ICSD ID: 4162.</p>
138	<p>α-[(CH₃)₄N]₄[V^VV^VW₁₁O₄₀]·4H₂O One V atom (addenda position) is disordered over 12 positions (0.08 V/0.92 W) Klevtsova, R. F.; Glinskaya, L. A.; Yurchenko, E. N.; Gutsul, T. D. <i>Kh. Strukt. Khim.</i> 1991, 82. CSD ID: JUJLUV.</p>
139	<p>α-[(CH₃)₄N]₇[V^VW₁₂O₄₀]·15H₂O Some water molecules are disordered; oxidation state of V atom perhaps wrong Khan, M. I.; Cevik, S.; Hayashi, R. <i>J. Chem. Soc., Dalton Trans.</i> 1999, 1651. CSD ID: FOBXEZ.</p>
140	<p>α-K₆H₃[ZnAlW₁₁O₄₀]·9.5H₂O Yang, Q.-H.; Fu, Q.; Liu, J.-F.; Xing, Y.; Lin, Y.-H.; Jia, H.-Q. <i>Chemical Research in Chinese Universities</i> 1997, 294.</p>
141	<p>α-K₆H₃[Zn^{II}Al^{III}W₁₁O₄₀]·9.5H₂O Al atom is disordered over 12 positions (0.042 Al/0.458 W); H counter-cations assumed for charge balance Yang, Q.-H.; Zhou, D. F.; Dai, H. C.; Liu, J. F.; Xing, Y. L.; Yong, H.; Jia, H. Q. <i>Polyhedron</i> 1997, 3985. ICSD ID: 85310.</p>
142	<p>α-[(Me)₄N]₄[H₂Zn^{II}Sn^{IV}W₁₁O₃₉]·9H₂O Wrong space group (P2₁/m) so used P2₁ instead; several coordinates recalculated: y-coord. of W(5), O(30), C(31), and C(34) now positive; z-coord. Of N(3) should be 0.9621 (not 0.6921); missing a bridging O atom between Sn and W; H atoms associated with POM assumed for charge balance Yang, Q.-H.; Dai, H.-C.; Liu, J.-F.; Xing, Y.; Lin, Y.-H.; Jia, H.-Q. <i>Chinese J. Struct. Chem. (Jiegou Huaxue)</i> 1998, 31. CSD ID: PALQOI.</p>

Table S2. Crystal Data and Structure Refinement for $\beta\text{-Cs}_{4.5}\text{K}_{0.5}\mathbf{1}$

formula	$\beta\text{-Cs}_{4.5}\text{K}_{0.5}[\text{AlW}_{12}\text{O}_{40}]\cdot 7.5\text{H}_2\text{O}$
crystal color, habit	colorless, prism
crystal size, mm ³	0.22 x 0.20 x 0.18
crystal system	orthorhombic, $\alpha = \beta = \gamma = 90^\circ$
space group	Pmc2 ₁
unit cell	
a, Å	16.0441(10)
b, Å	13.2270(8)
c, Å	20.5919(13)
V, Å ³	4369.9(5)
Z	4
fw	3610.82
D_{calc} , Mg/m ³	5.488
μ , mm ⁻¹	35.324
F(000)	6152
diffractometer	Bruker D8 SMART APEX CCD
$\lambda(\text{MoK}_\alpha \text{ (graphite)})$, Å	0.71073
T, K	100(2)
θ range, deg	1.54 to 33.03
index ranges	-23 < h < 24 -19 < k < 19 -31 < l < 31
total no. of data	76106
indep. reflns.	16190 ($R_{\text{int}} = 0.0615$)
syst. used	SHELXTL-V5.10
abs. correction	Semi-empirical from equivalents and face-indexing
max. and min. transmission	1.000 and 0.482561
refinement method	Full-matrix least squares on F^2
no. of obsd. data ($I > 2\sigma(I)$)	16190
no. of restraints	1
no. of params.	419
$R1^a$ ($I > 2\sigma(I)$)	0.0554
$wR2^b$ ($I > 2\sigma(I)$)	0.1231
GOF on F^2	1.166
Largest diff peak and hole, e Å ⁻³	11.063 and -11.458

$$^a R1 = \Sigma ||F_o| - |F_c|| / |F_o|. \quad ^b wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}.$$

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-Cs}_{4.5}\text{K}_{0.5}\mathbf{1}$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
<u>Molecule 1</u>				
W(1)	6032(1)	13309(1)	9687(1)	9(1)
W(2)	5000	11559(1)	10500(1)	12(1)
W(3)	6180(1)	13171(1)	7913(1)	10(1)
W(4)	7189(1)	11439(1)	8731(1)	12(1)
W(5)	3976(1)	9458(1)	9652(1)	16(1)
W(6)	6153(1)	10803(1)	7408(1)	9(1)
W(7)	5000	8852(1)	8331(1)	14(1)
Al(1)	5000	11417(5)	8808(4)	5(1)
O(1)	6700(11)	14211(11)	9982(8)	17(3)
O(2)	5000	11352(17)	11342(12)	20(5)
O(3)	6419(10)	14301(11)	7529(8)	18(3)
O(4)	8223(11)	11377(12)	8924(9)	22(3)
O(5)	3281(13)	8805(13)	10116(10)	26(4)
O(6)	6564(10)	10309(11)	6692(8)	15(3)
O(7)	5000	7761(14)	7897(10)	10(3)
O(8)	5000	14041(15)	9842(10)	11(4)
O(9)	5841(9)	12614(10)	10486(7)	9(2)
O(10)	5998(9)	13622(9)	8796(7)	9(2)
O(11)	6787(9)	12262(10)	9439(7)	11(2)
O(12)	4171(12)	10630(12)	10188(8)	20(3)
O(13)	5000	13227(12)	7755(9)	5(3)
O(14)	7213(10)	12708(11)	8234(8)	15(3)
O(15)	5000	8948(16)	10045(10)	14(4)
O(16)	3242(11)	10238(11)	9145(8)	17(3)
O(17)	6331(9)	12258(10)	7217(7)	11(2)
O(18)	7198(9)	10792(10)	7873(7)	12(2)
O(19)	5846(10)	8500(11)	8967(8)	16(3)
O(20)	5000	11020(20)	7171(13)	28(6)
O(21)	5794(10)	9618(11)	7823(7)	15(3)
O(22)	5000	12219(13)	9507(9)	7(3)
O(23)	5875(9)	11629(9)	8333(7)	9(2)
O(24)	5000	10127(13)	9036(9)	8(3)
<u>Molecule 2</u>				
W(8)	8966(1)	8191(1)	7439(1)	10(1)
W(9)	10000	6427(1)	6644(1)	11(1)
W(10)	8824(1)	8077(1)	9209(1)	11(1)
W(11)	7806(1)	6340(1)	8420(1)	11(1)
W(12)	8976(1)	4348(1)	7504(1)	11(1)
W(13)	8840(1)	5722(1)	9746(1)	10(1)
W(14)	10000	3758(1)	8832(1)	10(1)
Al(2)	10000	6287(6)	8355(4)	8(1)
O(25)	8277(10)	9102(10)	7149(7)	11(2)
O(26)	10000	6167(14)	5833(9)	9(3)
O(27)	8479(8)	9163(9)	9587(6)	9(2)

O(28)	6756(9)	6247(10)	8213(7)	11(3)
O(29)	8288(10)	3659(11)	7045(8)	14(3)
O(30)	8478(9)	5241(10)	10468(7)	12(3)
O(31)	10000	2626(17)	9263(12)	20(4)
O(32)	10000	8936(14)	7309(9)	8(3)
O(33)	9154(9)	7483(10)	6628(7)	13(3)
O(34)	9076(9)	8548(10)	8356(8)	11(2)
O(35)	8226(8)	7130(10)	7705(7)	9(2)
O(36)	9200(9)	5527(10)	6955(7)	9(2)
O(37)	10000	8093(15)	9367(11)	15(4)
O(38)	7769(8)	7612(9)	8883(6)	6(2)
O(39)	8261(9)	5181(9)	8004(7)	9(2)
O(40)	10000	3827(15)	7170(10)	13(4)
O(41)	8680(9)	7104(11)	9922(7)	12(3)
O(42)	7824(9)	5704(10)	9244(7)	9(2)
O(43)	9156(10)	3411(11)	8213(8)	16(3)
O(44)	10000	5904(12)	9932(8)	1(3)
O(45)	9164(7)	4534(8)	9291(5)	1(2)
O(46)	10000	7053(13)	7674(9)	6(3)
O(47)	9098(9)	6542(10)	8808(7)	10(2)
O(48)	10000	4958(13)	8119(9)	7(3)
Cs(1)	8443(1)	12754(1)	10216(1)	13(1)
Cs(2)	10000	10568(1)	8651(1)	17(1)
Cs(3)	6474(1)	7531(2)	6965(1)	63(1)
Cs(4)	5000	5772(1)	8700(1)	20(1)
Cs(5)	5000	12736(2)	6011(1)	24(1)
Cs(6)	7812(1)	7909(1)	11128(1)	26(1)
K(1)	10000	10583(6)	6571(3)	26(1)
O(1W)	7307(10)	8856(14)	5910(10)	30(4)
O(2W)	7581(15)	6012(18)	6427(12)	43(5)
O(3W)	8857(11)	8651(14)	12436(10)	27(4)
O(4W)	6269(16)	6506(16)	9832(17)	59(9)
O(5W)	10000	12354(16)	6091(12)	17(4)
O(6W)	8844(14)	9858(18)	5732(11)	46(5)
O(7W)	5470(30)	14980(30)	6030(20)	40(9)
O(8W)	7142(17)	7074(19)	11044(13)	32(5)
O(9W)	8090(90)	9750(110)	11640(70)	40(30)
O(10W)	5366(17)	5740(20)	7089(13)	31(6)
O(11W)	6620(20)	14100(30)	6156(19)	34(8)
O(12W)	0	8870(50)	5320(30)	34(14)
O(13W)	7030(30)	5170(30)	6360(20)	37(10)

Table S4. Selected Bond Distances (Å) and Angles (deg) for β -Cs_{4.5}K_{0.5}**1** (Molecule 1)

Distances			
Al(1)—O(22) ^a	1.787(19)	W(1)—O(9) ^d	1.910(14)
Al(1)—O(23) ^a	1.734(15)	W(1a)—O(8) ^d	1.945(10)
Al(1)—O(23a) ^a	1.734(15)	W(1a)—O(9a) ^d	1.910(14)
Al(1)—O(24) ^a	1.770(19)	W(2)—O(9) ^d	1.941(14)
W(1)—O(22) ^b	2.227(12)	W(2)—O(9a) ^d	1.941(14)
W(1a)—O(22) ^b	2.227(12)	W(1)—O(10) ^e	1.882(15)
W(2)—O(22) ^b	2.223(18)	W(1)—O(11) ^e	1.909(14)
W(1)—O(1) ^c	1.715(17)	W(1a)—O(10a) ^e	1.882(15)
W(1a)—O(1a) ^c	1.715(17)	W(1a)—O(11a) ^e	1.909(14)
W(2)—O(2) ^c	1.76(2)	W(2)—O(12) ^e	1.922(18)
W(1)—O(8) ^d	1.945(10)	W(2)—O(12a) ^e	1.922(17)
Angles			
O(22)—Al(1)—O(23) ^f	111.0(6)	W(1)—O(10)—W(3) ⁱ	147.5(7)
O(22)—Al(1)—O(23a) ^f	111.0(6)	W(1)—O(11)—W(4) ⁱ	145.4(8)
O(22)—Al(1)—O(24) ^f	111.0(9)	W(1a)—O(10a)—W(3a) ⁱ	147.5(7)

O(23)—Al(1)—O(23a) ^f	108.1(10)	W(1a)—O(11a)—W(4a) ⁱ	145.4(8)
O(23)—Al(1)—O(24) ^f	107.8(6)	W(2)—O(12)—W(5) ⁱ	144.9(10)
O(23a)—Al(1)—O(24) ^f	107.8(6)	W(2)—O(12a)—W(5a) ⁱ	144.9(10)
Al(1)—O(22)—W(1) ^g	121.2(6)	W(3)—O(13)—W(3a) ^j	160.1(10)
Al(1)—O(22)—W(1a) ^g	121.2(6)	W(4)—O(16a)—W(5a) ^j	156.9(9)
Al(1)—O(22)—W(2) ^g	120.5(9)	W(4a)—O(16)—W(5) ^j	156.9(9)
W(1)—O(8)—W(1a) ^h	116.7(10)	W(6)—O(20)—W(6a) ^j	145.9(15)
W(1)—O(9)—W(2) ^h	118.0(7)	W(6)—O(21)—W(7) ^j	152.4(9)
W(1a)—O(9a)—W(2) ^h	118.0(7)	W(6a)—O(21a)—W(7a) ^j	152.4(9)

Distances between ^aAl—μ₄-O, ^bW—μ₄-O (rotated W₃O₁₃ unit), ^cW—terminal-O (rotated triad), ^dW—μ-O (intra-rotated triad), ^eW—μ-O (inter-triad from rotated to non-rotated). Angles between ^fμ₄-O—Al—μ₄-O, ^gAl—μ₄-O—W (rotated triad), ^hW—μ-O—W (intra-rotated triad), ⁱW—μ-O—W (inter-triad from rotated to non-rotated), ^jW—μ-O—W (inter-triad from non-rotated to non-rotated).

Table S5. Selected Bond Distances (Å) and Angles (deg) for β-Cs_{4.5}K_{0.5}**1** (Molecule 2)

Distances			
Al(2)—O(46) ^a	1.728(19)	W(8)—O(33) ^d	1.938(15)
Al(2)—O(47) ^a	1.755(15)	W(8a)—O(32) ^d	1.947(10)
Al(2)—O(47a) ^a	1.755(15)	W(8a)—O(33a) ^d	1.938(15)
Al(2)—O(48) ^a	1.82(2)	W(9)—O(33) ^d	1.949(14)
W(8)—O(46) ^b	2.292(12)	W(9)—O(33a) ^d	1.949(14)
W(8a)—O(46) ^b	2.292(12)	W(8)—O(34) ^e	1.955(15)
W(9)—O(46) ^b	2.277(18)	W(8)—O(35) ^e	1.919(13)
W(8)—O(25) ^c	1.740(15)	W(8a)—O(34a) ^e	1.955(15)
W(8a)—O(25a) ^c	1.740(15)	W(8a)—O(35a) ^e	1.919(13)
W(9)—O(26) ^c	1.71(2)	W(9)—O(36) ^e	1.864(14)
W(8)—O(32) ^d	1.947(10)	W(9)—O(36a) ^e	1.864(14)
Angles			
O(46)—Al(2)—O(47) ^f	108.6(6)	W(8)—O(34)—W(10) ⁱ	142.4(7)
O(46)—Al(2)—O(47a) ^f	108.6(6)	W(8)—O(35)—W(11) ⁱ	146.2(8)
O(46)—Al(2)—O(48) ^f	110.5(9)	W(8a)—O(34a)—W(10a) ⁱ	142.4(7)
O(47)—Al(2)—O(47a) ^f	111.0(11)	W(8a)—O(35a)—W(11a) ⁱ	146.2(8)

O(47)—Al(2)—O(48) ^f	109.1(6)	W(9)—O(36)—W(12) ⁱ	146.4(8)
O(47a)—Al(2)—O(48) ^f	109.1(6)	W(9)—O(36a)—W(12a) ⁱ	146.4(8)
Al(2)—O(46)—W(8) ^g	123.8(6)	W(10)—O(37)—W(10a) ^j	160.4(13)
Al(2)—O(46)—W(8a) ^g	123.8(6)	W(11)—O(39)—W(12) ^j	161.1(8)
Al(2)—O(46)—W(9) ^g	122.8(9)	W(11a)—O(39a)—W(12a) ^j	161.1(8)
W(8)—O(32)—W(8a) ^h	116.8(9)	W(13)—O(44)—W(13a) ^j	152.7(9)
W(8)—O(33)—W(9) ^h	116.1(7)	W(13)—O(45)—W(14) ^j	150.3(7)
W(8a)—O(33a)—W(9) ^h	116.1(7)	W(13a)—O(45a)—W(14) ^j	150.3(7)

Distances between ^aAl—μ₄-O, ^bW—μ₄-O (rotated W₃O₁₃ unit), ^cW—terminal-O (rotated triad), ^dW—μ-O (intra-rotated triad), ^eW—μ-O (inter-triad from rotated to non-rotated). Angles between ^fμ₄-O—Al—μ₄-O, ^gAl—μ₄-O—W (rotated triad), ^hW—μ-O—W (intra-rotated triad), ⁱW—μ-O—W (inter-triad from rotated to non-rotated), ^jW—μ-O—W (inter-triad from non-rotated to non-rotated).

Table S6. Crystal Data and Structure Refinement for β-Cs_{3.5}K_{1.5}**1**

formula	β-Cs _{3.5} K _{1.5} [AlW ₁₂ O ₄₀]·5H ₂ O
crystal color, habit	colorless, prism
crystal size, mm ³	0.39 x 0.36 x 0.22
crystal system	rhombohedral (a = b ≠ c; α = β = 90°, γ = 120°)
space group	R-3c
unit cell	
a, Å	17.4163(8)
c, Å	47.663(5)
V, Å ³	12520.5(14)
Z	12
fw	3476.22
D _{calc} , Mg/m ³	5.532
μ, mm ⁻¹	36.219
F(000)	17779
diffractometer	Bruker D8 SMART APEX CCD
λ(MoK _α (graphite)), Å	0.71073
T, K	100(2)
θ range, deg	1.60 to 33.08
index ranges	-26 < h < 26 -26 < k < 26 -72 < l < 71
total no. of data	63716
indep. reflns.	4999 (R _{int} = 0.1047)
syst. used	SHELXTL-V5.10
abs. correction	Semi-empirical from equivalents
max. and min. transmission	1.000 and 0.346362
refinement method	Full-matrix least squares on F ²

no. of obsd. data ($I > 2\sigma(I)$)	4999
no. of restraints	0
no. of params.	189
$R1^a$ ($I > 2\sigma(I)$)	0.0865
$wR2^b$ ($I > 2\sigma(I)$)	0.2202
GOF on F^2	1.114
Largest diff peak and hole, $e \text{ \AA}^{-3}$	8.302 and -9.085

^a $R1 = \Sigma ||F_o| - |F_c|| / |F_o|$. ^b $wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}$.

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for β -Cs_{3.5}K_{1.5}**1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	2553(1)	7127(1)	8677(1)	9(1)
W(2)	2799(1)	8361(1)	8031(1)	14(1)
W(3)	1181(1)	6329(1)	8049(1)	15(1)
W(4)	2374(1)	7093(1)	7475(1)	19(1)
Al(1)	3333	6667	8055(2)	5(1)
O(1)	2018(9)	7430(8)	8916(3)	13(2)
O(2)	2869(11)	9365(11)	8071(3)	21(3)
O(3)	59(9)	5891(12)	8092(4)	26(4)
O(4)	2079(13)	7222(12)	7140(3)	29(4)
O(5)	3333	6667	8416(5)	12(4)
O(6)	2616(9)	7012(9)	7932(3)	13(2)
O(7)	3689(9)	7685(8)	8842(2)	10(2)
O(8)	1598(8)	6434(9)	8420(3)	9(2)
O(9)	2905(8)	8044(9)	8410(3)	10(2)
O(10)	1558(10)	7573(10)	8072(3)	17(3)
O(11)	4056(9)	8771(9)	7991(3)	13(2)
O(12)	1233(10)	6507(10)	7645(3)	20(3)
O(13)	2626(10)	8236(10)	7636(3)	20(3)
O(14)	3650(10)	7629(10)	7436(3)	18(3)
Cs(1)	-1103(2)	3860(2)	8148(1)	39(1)
Cs(2)	3542(2)	9421(2)	9040(1)	49(1)
K(1)	376(5)	6667	9167	32(2)
O(1W)	1120(20)	7740(20)	9565(7)	48(7)
O(2W)	-1200(20)	6667	9167	56(12)
O(3W)	4000(30)	9670(30)	8678(12)	47(12)

Table S8. Selected Bond Distances (Å) and Angles (deg) for β -Cs_{3.5}K_{1.5}**1**

Distances			
Al(1)—O(5) ^a	1.72(2)	W(1)—O(7b) ^d	1.950(13)
Al(1)—O(6) ^a	1.736(14)	W(1a)—O(7) ^d	1.885(13)
Al(1)—O(6a) ^a	1.736(14)	W(1a)—O(7a) ^d	1.950(13)
Al(1)—O(6b) ^a	1.736(14)	W(1b)—O(7a) ^d	1.950(13)
W(1)—O(5) ^b	2.265(12)	W(1b)—O(7b) ^d	1.950(13)
W(1a)—O(5) ^b	2.265(12)	W(1)—O(8) ^e	1.929(12)
W(1b)—O(5) ^b	2.265(12)	W(1)—O(9) ^e	1.890(13)
W(1)—O(1) ^c	1.711(13)	W(1a)—O(8a) ^e	1.929(12)
W(1a)—O(1a) ^c	1.711(13)	W(1a)—O(9a) ^e	1.890(13)
W(1b)—O(1b) ^c	1.711(13)	W(1b)—O(8b) ^e	1.929(12)
W(1)—O(7) ^d	1.885(13)	W(1b)—O(9b) ^e	1.890(13)
Angles			
O(5)—Al(1)—O(6) ^f	109.6(5)	W(1)—O(9)—W(2) ⁱ	147.1(7)
O(5)—Al(1)—O(6a) ^f	109.6(5)	W(1)—O(8)—W(3) ⁱ	145.7(7)
O(5)—Al(1)—O(6b) ^f	109.6(5)	W(1a)—O(9a)—W(2a) ⁱ	147.1(7)
O(6)—Al(1)—O(6a) ^f	109.3(5)	W(1a)—O(8a)—W(3a) ⁱ	145.7(7)
O(6)—Al(1)—O(6b) ^f	109.3(5)	W(1b)—O(9b)—W(2b) ⁱ	147.1(7)
O(6a)—Al(1)—O(6b) ^f	109.3(5)	W(1b)—O(8b)—W(3b) ⁱ	145.7(7)
Al(1)—O(5)—W(1) ^g	123.4(5)	W(2)—O(11)—W(3a) ^j	158.3(8)
Al(1)—O(5)—W(1a) ^g	123.4(5)	W(2a)—O(11a)—W(3b) ^j	158.3(8)
Al(1)—O(5)—W(1b) ^g	123.4(5)	W(2b)—O(11b)—W(3) ^j	158.3(8)
W(1)—O(7)—W(1a) ^h	117.4(6)	W(4)—O(14)—W(4a) ^j	152.8(9)
W(1)—O(7b)—W(1b) ^h	117.4(6)	W(4)—O(14b)—W(4b) ^j	152.8(9)
W(1a)—O(7a)—W(1b) ^h	117.4(6)	W(4a)—O(14a)—W(4b) ^j	152.8(9)

Distances between ^aAl—μ₄-O, ^bW—μ₄-O (rotated W₃O₁₃ unit), ^cW—terminal-O (rotated triad), ^dW—μ-O (intra-rotated triad), ^eW—μ-O (inter-triad from rotated to non-rotated). Angles between ^fμ₄-O—Al—μ₄-O, ^gAl—μ₄-O—W (rotated triad), ^hW—μ-O—W (intra-rotated triad), ⁱW—μ-O—W (inter-triad from rotated to non-rotated), ^jW—μ-O—W (inter-triad from non-rotated to non-rotated).

Table S9. Crystal Data and Structure Refinement for β -K₅1

formula	β -K ₅ [AlW ₁₂ O ₄₀]·8 H ₂ O
crystal color, habit	colorless, plate
crystal size, mm ³	0.14 x 0.11 x 0.02
crystal system	orthorhombic, $\alpha = \beta = \gamma = 90^\circ$
space group	Pnma
unit cell	
a, Å	19.8499(17)
b, Å	15.5825(13)
c, Å	12.9329(11)
V, Å ³	4000.3(6)
Z	4
fw	3610.82
D_{calc} , Mg/m ³	5.308
μ , mm ⁻¹	35.021
F(000)	5520
diffractometer	Bruker D8 SMART APEX CCD
λ (MoK $_{\alpha}$ (graphite)), Å	0.71073
T, K	100(2)
θ range, deg	1.88 to 23.26
index ranges	-22 < h < 22
	-17 < k < 17
	-14 < l < 14
total no. of data	29324
indep. reflns.	3001 ($R_{\text{int}} = 0.1289$)
syst. used	SHELXTL-V5.10
abs. correction	Semi-empirical from equivalents
max. and min. transmission	1.000 and 0.079089
refinement method	Full-matrix least squares on F ²
no. of obsd. data ($I > 2\sigma(I)$)	3001
no. of restraints	0
no. of params.	218
R1 ^a ($I > 2\sigma(I)$)	0.0856
wR2 ^b ($I > 2\sigma(I)$)	0.1818
GOF on F ²	1.267
Largest diff peak and hole, e Å ⁻³	4.843 and -4.099

$$^a R1 = \Sigma ||F_o| - |F_c|| / |F_o|. \quad ^b wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{0.5}.$$

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for β -K₅1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	3654(1)	1435(1)	5849(1)	12(1)
W(2)	1324(1)	1316(1)	3200(1)	13(1)
W(3)	2311(1)	2500	1254(2)	15(1)
W(4)	3688(1)	1444(1)	1917(1)	12(1)
W(5)	2696(1)	245(1)	3907(1)	12(1)
W(6)	1830(1)	1289(1)	5641(1)	12(1)
W(7)	4522(1)	2500	4074(1)	11(1)
Al(1)	2773(7)	2500	3838(11)	10(3)
O(7)	3476(17)	2500	4660(30)	16(8)
O(12)	2298(12)	1595(16)	4074(18)	16(6)
O(14)	3039(15)	2500	2580(20)	5(7)
O(1)	3951(12)	765(16)	6784(18)	15(5)
O(2)	3734(16)	2500	6590(20)	8(7)
O(3)	4517(13)	1635(16)	5141(19)	20(6)
O(4)	5378(19)	2500	3930(30)	22(9)
O(5)	2714(10)	1537(13)	6184(16)	4(5)
O(6)	3422(12)	644(16)	4773(18)	16(6)
O(8)	4238(11)	1632(14)	3109(17)	8(5)
O(9)	1395(13)	983(18)	6770(20)	24(6)
O(10)	2166(11)	223(14)	5152(16)	7(5)
O(11)	2879(12)	-831(16)	3812(19)	19(6)
O(13)	3153(11)	697(14)	2738(16)	8(5)
O(15)	4191(12)	748(15)	1241(18)	14(5)
O(16)	4105(17)	2500	1440(30)	16(8)
O(17)	1106(13)	1099(17)	4650(20)	24(6)
O(18)	1888(15)	264(19)	3220(20)	32(7)
O(19)	1130(20)	2500	3420(30)	27(9)
O(20)	1815(11)	1669(14)	1986(17)	10(5)
O(21)	2994(13)	1621(16)	895(19)	18(6)
O(22)	597(13)	894(17)	2700(20)	23(6)
O(23)	1895(17)	2500	90(20)	12(7)
O(24)	1657(17)	2500	5690(30)	15(8)
K(1)	2409(9)	2500	8086(10)	37(4)
K(2)	5897(5)	1034(7)	4831(8)	41(3)
K(3)	4927(11)	380(16)	-433(17)	51(6)
K(4)	4415(14)	2500	8320(20)	38(7)
K(5)	4961(18)	2500	9800(30)	67(11)
O(1W)	5252(17)	30(20)	6260(30)	47(9)
O(2W)	3547(18)	1460(20)	8850(30)	52(9)
O(3W)	5180(80)	2500	11530(120)	40(40)
O(4W)	970(30)	2060(40)	8320(50)	35(14)
O(5W)	5170(30)	1600(40)	-2350(50)	40(16)
O(6W)	3300(40)	-1280(50)	4760(60)	60(20)
O(7W)	3670(50)	940(60)	10180(70)	40(20)

Table S11. Selected Bond Distances (Å) and Angles (deg) for β -K₅**1**

Distances			
Al(1)—O(7) ^a	1.75(4)	W(1)—O(3) ^d	1.97(3)
Al(1)—O(12) ^a	1.72(3)	W(1a)—O(2) ^d	1.923(16)
Al(1)—O(12a) ^a	1.72(3)	W(1a)—O(3a) ^d	1.97(3)
Al(1)—O(14) ^a	1.71(3)	W(7)—O(3) ^d	1.93(3)
W(1)—O(7) ^b	2.29(2)	W(7)—O(3a) ^d	1.93(3)
W(1a)—O(7) ^b	2.29(2)	W(1)—O(5) ^e	1.92(2)
W(7)—O(7) ^b	2.21(3)	W(1)—O(6) ^e	1.92(2)
W(1)—O(1) ^c	1.70(2)	W(1a)—O(5a) ^e	1.92(2)
W(1a)—O(1a) ^c	1.70(2)	W(1a)—O(6a) ^e	1.92(2)
W(7)—O(4) ^c	1.71(4)	W(7)—O(8) ^e	1.92(2)

W(1)—O(2) ^d	1.923(16)	W(7)—O(8a) ^e	1.92(2)
Angles			
O(7)—Al(1)—O(12) ^f	109.2(11)	W(1)—O(5)—W(6) ⁱ	141.6(12)
O(7)—Al(1)—O(12a) ^f	109.2(11)	W(1)—O(6)—W(5) ⁱ	144.0(14)
O(7)—Al(1)—O(14) ^f	109.3(17)	W(1a)—O(5a)—W(6a) ⁱ	141.6(12)
O(12)—Al(1)—O(12a) ^f	109.8(18)	W(1a)—O(6a)—W(5a) ⁱ	144.0(14)
O(12)—Al(1)—O(14) ^f	109.7(11)	W(7)—O(8)—W(4) ⁱ	142.9(12)
O(12a)—Al(1)—O(14) ^f	109.7(11)	W(7)—O(8a)—W(4a) ⁱ	142.9(12)
Al(1)—O(7)—W(1) ^g	122.0(11)	W(2)—O(19)—W(2a) ^j	151(2)
Al(1)—O(7)—W(1a) ^g	122.0(11)	W(2)—O(20)—W(3) ^j	150.5(13)
Al(1)—O(7)—W(7) ^g	122.7(18)	W(2a)—O(20a)—W(3) ^j	150.5(13)
W(1)—O(2)—W(1a) ^h	119.2(16)	W(4)—O(13)—W(5) ^j	160.0(13)
W(1)—O(3)—W(7) ^h	116.6(13)	W(4a)—O(13a)—W(5a) ^j	160.0(13)
W(1a)—O(3a)—W(7) ^h	116.6(13)	W(6)—O(24)—W(6a) ^j	159(2)

Distances between ^aAl—μ₄-O, ^bW—μ₄-O (rotated W₃O₁₃ unit), ^cW—terminal-O (rotated triad), ^dW—μ-O (intra-rotated triad), ^eW—μ-O (inter-triad from rotated to non-rotated). Angles between ^fμ₄-O—Al—μ₄-O, ^gAl—μ₄-O—W (rotated triad), ^hW—μ-O—W (intra-rotated triad), ⁱW—μ-O—W (inter-triad from rotated to non-rotated), ^jW—μ-O—W (inter-triad from non-rotated to non-rotated).

Table S12. Mean^a Distances (Å) and Angles (deg) from Crystallographic Data Acquired using Crystals of Three Different β-[AlW₁₂O₄₀]⁵⁻ Salts from Three Different Solutions

Isomer	R-Value	X—μ ₄ -O	μ ₄ -O—W	Sum of X—μ ₄ -O and μ ₄ -O—W	μ ₄ -O—X—μ ₄ -O
β-Cs _{4.5} K _{0.5} ^b	0.0554	1.760(17)	2.245(14)	4.00(2)	109.5(7)
β-Cs _{3.5} K _{1.5}	0.0865	1.732(16)	2.250(13)	3.98(2)	109.5(5)
β-K ₅	0.0856	1.73(3)	2.27(2)	4.00(4)	109.5(14)

^aAverage values with uncertainties (one sigma) in parentheses. ^bThis structure is shown in Fig. 2.

Evaluation of previously reported β-[SiW₁₂O₄₀]⁴⁻ Crystal Structures. In the two published structures for which fractional atomic coordinates are available (Matsumoto, K. Y.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Japan* 1975, 3146. and Fuchs, J.; Thiele, A.; Palm, R. *Z. Naturforsch., Teil B* 1981, 161.) distortion of the central [SiO₄]⁴⁻ tetrahedron is reported. In Matsumoto et al., (R₁ = 13.8), Si—μ₄-O distances ranged from 1.37 to 1.83 Å, and O—Si—O angles ranged from 99 to 116°. Notably, uncertainties in atomic coordinates were quite large: reported

distances for the three crystallographically distinct Si–O bonds were 1.37(17), 1.83(9) and 1.64(8) Å. Jeanin and co-workers (Robert, F.; Tezé, A.; Hervé, G.; Jeanin, Y. *Acta Cryst. B* 1980, 11.) attributed distortion within the SiO₄ moiety in the structure of β -2 reported by Matsumoto (1975) to a “less well refined structure”. In the second case, (Fuchs, 1981), an R_1 value of 10.6 was obtained, and considerably less distortion of the [SiO₄]⁴⁻ moiety was reported: Si– μ_4 -O distances ranged from 1.63 to 1.84 Å and O–Si–O angles ranged from 99 to 116°. Nonetheless, the authors stated that large uncertainties in W–O bond distances (up to 0.06 Å, apparently due to uncertainties in positions of the lighter O atoms), precluded publication of a table of bond lengths. Uncertainties in Si–O bond distances (both light elements), were probably even larger. In the earliest published structure, (Yamamura, K.; Sasaki, Y. *J. Chem. Soc. Chem. Commun.* 1973, 648.) an R_1 value of 14.7 was obtained and no fractional atomic coordinates, bonds distances or angles were reported.

Preparation of X-ray Quality Crystals

β -Cs_{4.5}K_{0.5}[AlW₁₂O₄₀]·7.5H₂O. To 2 mL of a 1 M CsCl solution was added 100 mg (3.26 x 10⁻⁵ mol) of β -K₅**1**. The resulting white precipitate was separated via filtration and dissolved in 2 mL water, covered with punctured parafilm, allowed to slowly evaporate for ~2 weeks at 25 °C, transferred to a refrigerator (~7 °C), and colorless prismatic crystals were observed after a few hours.

β -Cs_{3.5}K_{1.5}[AlW₁₂O₄₀]·5H₂O. To 100 mg (3.26 x 10⁻⁵ mol) of β -K₅**1** was added ~2 mL of a 1 M aqueous solution of CsCl. The resulting white precipitate was separated via filtration and dissolved in 2 mL water, covered with punctured parafilm, and allowed to slowly evaporate at 25 °C. Initially long, thin, colorless, needle-like crystals formed which were not of X-ray quality. The solution was left to continue evaporating and eventually colorless, X-ray quality, prismatic crystals formed.

β -K₅[AlW₁₂O₄₀]·3 H₂O. 10.00 g (3.04 x 10⁻³ mol) of Na₅**1** (mixture of α and β isomers) was dissolved in ~25 mL of a 1 M aqueous solution of KCl, covered with punctured parafilm, and allowed to slowly evaporate at 25 °C. As colorless crystals formed they were removed by filtration via suction and analyzed by ²⁷Al NMR spectroscopy to determine isomeric purity. This fractional crystallization process was continued until all of the α isomer had been separated (crystallized first) and only the β isomer remained in solution. Small, colorless, X-ray quality, plate-like crystals were grown from the final solution after several fractions of α were removed.

X-ray Crystallographic Studies.

Instrumentation and Methods. Single crystals of β -Cs_{4.5}K_{0.5}[AlW₁₂O₄₀]·7.5H₂O, β -Cs_{3.5}K_{1.5}[AlW₁₂O₄₀]·5H₂O, and β -K₅[AlW₁₂O₄₀]·8H₂O, suitable for X-ray analysis, were each coated with Paratone oil, suspended in a small fiber loop and placed in a cooled nitrogen gas stream at 100(2)K on a Bruker D8 SMART APEX CCD sealed tube diffractometer. Diffraction intensities were measured using graphite-monochromated MoK α radiation (λ = 0.71073 Å) and a combination of ϕ and ω scans with 10 s frames traversing about ω at 0.3° increments. Data collection, indexing, and initial cell refinements were carried out using SMART (Version 5.624, 2000, Bruker AXS, Inc., Madison, WI); frame integration and final cell refinements were done using SAINT (Version 6.02, 2000, Bruker AXS, Inc.). The molecular structure of each complex was determined using direct methods and Fourier techniques and refined by full-matrix least squares (SHELXTL Version 5.10, 2000, Bruker AXS, Inc.). A multiple absorption correction for each data set was applied using the program SADABS (Version 2.03, 2001, George Sheldrick, University of Göttingen). The largest residual electron density for each structure was located close to (less than 1.0 σ) the W addenda atoms and the Cs atoms (in β -Cs_{4.5}K_{0.5}**1** and β -Cs_{3.5}K_{1.5}**1**) and was most likely due to imperfect absorption corrections often encountered in

heavy-metal atom structures. Additional details of data collection and structure refinement are given in Tables S1-S10 and the CIF files.

β -Cs_{4.5}K_{0.5}[AlW₁₂O₄₀]·7.5H₂O. The crystal faces were indexed and the additional absorption corrections made in XPREP (SHELXTL Version 5.10). Each W, Cs, and K atom, as well as O(1w), O(3w), and O(4w) (solvent waters) were refined using anisotropic thermal parameters. All remaining atoms (Al, O atoms within the Keggin anion, and waters of hydration O atoms) were refined using isotropic thermal parameters. Some solvent waters were disordered within the crystal lattice and were refined with partial occupancy (O(5w), 0.5; O(7w), 0.5; O(8w), 0.8; O(9w), 0.15; O(10w), 0.65; O(11w), 0.5; O(12w), 0.2; O(13w), 0.45).

β -Cs_{3.5}K_{1.5}[AlW₁₂O₄₀]·5H₂O. Each W, Cs, and K atom, as well as some O atoms within the Keggin anion (terminal, O(1)-O(4); μ_4 , O(5)-O(6); μ , O(7)-O(11)) and O(2w) and O(3w) (solvent waters) were refined with anisotropic thermal parameters. All remaining atoms (Al, μ -O atoms within Keggin (O(12)-O(14)), and O(1w)) were refined using isotropic thermal parameters. Some atoms were disordered within the crystal lattice and were refined with partial occupancy (Cs(1), 0.633; Cs(2), 0.533; O(1w), 0.75; O(2w), 0.4; O(3w), 0.5).

β -K₅[AlW₁₂O₄₀]·8H₂O. Each W and K atom, as well as O(1w) (solvent water) were refined with anisotropic thermal parameters. All remaining atoms (Al, O atoms within the Keggin anion, O(2w), O(3w), O(4w), O(5w), O(6w), O(7w)) were refined with isotropic thermal parameters. Some atoms were disordered within the crystal lattice and were refined with partial occupancy (K(3), 0.5; K(4), 0.25; K(5), 0.25; O(3w), 0.15; O(4w), 0.5; O(5w), 0.5; O(6w), 0.5; O(7w), 0.35).