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Supplementary material for

An unprecedented ι-type octamolybdate: $[TbI_1]_2[(\beta\text{-}Mo_8O_{26})_{0.5}(\iota\text{-}Mo_8O_{26})]$ directed by a new tricationic template

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Experimental details

The IR spectra were recorded on a Shimazu IR435 spectrometer as KBr disk (4000–400 cm^{-1}). The purity of the bulk microcrystalline materials obtained from the syntheses was checked by Powder X-ray diffraction analysis. XRPD patterns were recorded using Cu Kα1 radiation on a PAN analytical X'Pert PRO diffractometer. Electrochemical measurements were performed with a CHI660b electrochemical workstation. A conventional three-electrode system was used. Ag/AgCl (3 M KCl) electrode was used as a reference electrode, and a Pt wire as a counter electrode. Chemically bulk-modified carbon-paste electrodes (CPEs) were used as the working electrodes.

Crystallographic data for the compound **1** was collected at 100(2)K on a Bruker APEX-II area-detector diffractometer equipped with graphite-monochromatized Mo-Ka radiation (λ = 0.71073Å). The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using

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geometrical constraint. The structure was refined with full-matrix least-squares techniques on F^2 using the SHELXTL-97 program package.

General method: Reagents and solvents for the syntheses were purchased from commercial sources and used without further purification. The tricationic TbI_1^{3+} was prepared as described in the literature(T. Fahlbusch, *et al*, *Eur. J. Org. Chem*., 2006, 1899.)

Synthesis of compound $[TbI_1]_2[(\beta\text{-}Mo_8O_{26})_{0.5}(\iota\text{-}Mo_8O_{26})]$ (**1**): A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.05 mmol), $TbI_1\cdot Br_3$ (0.05 mmol), and H_2O (10 mL) was stirred at room temperature until it was homogeneous, and adjusted by CH_3COOH to pH=4. Then the mixture was sealed in an 18 mL Teflon-lined stainless steel container, which was heated to 155°C under autogenously pressure for 4d. After slow cooling to room temperature with the rate $10°C\cdot h^{-1}$, the colorless, bulk crystals were formed. The products are not soluble in common solvents. IR (KBr, cm^{-1}): 3444 (m), 3093 (s), 1581 (w), 1561 (s), 1443 (s), 1383 (w), 1357 (m), 1326 (s), 1253 (w), 1172 (s), 1148 (s), 1024 (w), 946 (s), 912 (s), 865 (w), 839 (m), 791(m), 745 (s), 654 (s), 613 (s), 556(s), 518(m).

Table S1. Selected bond distances(Å) and angles(°)for compound **1**

Compound **1**			
Mo1—O4	1.689(4)	Mo7—O27	1.689(4)
Mo1—O13	1.740(4)	Mo7—O16	1.705(4)
Mo1—O3	1.934(4)	Mo7—O21	1.921(4)
Mo1—O5	1.959(4)	Mo7—O14	1.934(4)
Mo1—O11	2.377(3)	Mo7—O19	2.305(4)
Mo2—O25	1.695(4)	Mo7—O17	2.385(4)
Mo2—O29	1.746(4)	Mo8—O23	1.703(5)
Mo2—O15	1.798(4)	Mo8—O37	1.707(4)
Mo2—O17	1.809(4)	Mo8—O32	1.810(4)
Mo3—O28	1.691(4)	Mo8—O35	1.828(4)
Mo3—O24	1.701(4)	Mo9—O26	1.705(4)

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Mo3—O14	1.894(4)	Mo9—O22	1.705(4)
Mo3—O35	1.977(4)	Mo9—O30	1.891(4)
Mo3—O17	2.317(4)	Mo9—O21	1.907(4)
Mo3—O18	2.318(4)	Mo9—O19	2.427(4)
Mo4—O34	1.697(4)	Mo9—O15	2.428(4)
Mo4—O18	1.748(4)	Mo10—O39	1.685(4)
Mo4—O19	1.803(4)	Mo10—O33	1.703(4)
Mo4—O20	1.811(4)	Mo10—O31	1.930(4)
Mo5—O1	1.696(4)	Mo10—O30	1.956(4)
Mo5—O2	1.705(4)	Mo10—O15	2.314(4)
Mo5—O12	1.898(4)	Mo10—O20	2.389(4)
Mo5—O3	2.356(4)	Mo11—O36	1.684(4)
Mo5—O11	2.369(4)	Mo11—O38	1.697(5)
Mo6—O7	1.697(4)	Mo11—O31	1.889(4)
Mo6—O6	1.706(4)	Mo11—O32	1.996(4)
Mo6—O10	1.894(4)	Mo11—O29	2.322(4)
Mo6—O11	2.287(4)	Mo11—O20	2.341(4)
Mo6—O5	2.356(4)	Mo12—O8	1.697(4)
Mo12—O10	1.926(4)	Mo12—O9	1.700(4)
Mo12—O13	2.284(4)	Mo12—O12	1.925(4)
Mo12—O11	2.489(3)	Mo1—O3—Mo5	111.54(15)
O4—Mo1—O13	104.16(18)	Mo1—O5—Mo6	108.70(16)
O4—Mo1—O3	102.43(17)	Mo6—O10—Mo12	117.4(2)
O13—Mo1—O3	97.56(17)	Mo6—O11—Mo5	163.20(17)
O4—Mo1—O5	99.98(17)	Mo6—O11—Mo1	97.75(14)
O13—Mo1—O5	95.88(17)	Mo5—O11—Mo1	97.00(12)
O3—Mo1—O5	150.09(15)	Mo6—O11—Mo12	86.10(12)
O4—Mo1—O11	175.04(16)	Mo5—O11—Mo12	85.56(11)
O13—Mo1—O11	80.65(15)	Mo1—O11—Mo12	91.26(12)

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O3—Mo1—O11	77.90(14)	Mo5—O12—Mo12	119.36(19)
O5—Mo1—O11	78.10(14)	Mo1—O13—Mo12	119.08(19)
O25—Mo2—O29	108.9(2)	Mo3—O14—Mo7	119.21(19)
O25—Mo2—O15	109.12(18)	Mo2—O15—Mo10	129.12(19)
O29—Mo2—O15	110.37(17)	Mo2—O15—Mo9	123.67(19)
O25—Mo2—O17	107.74(19)	Mo10—O15—Mo9	89.90(13)
O29—Mo2—O17	108.60(18)	Mo2—O17—Mo3	147.6(2)
O15—Mo2—O17	112.01(18)	Mo2—O17—Mo7	122.97(17)
O28—Mo3—O24	103.67(18)	Mo3—O17—Mo7	89.21(13)
O28—Mo3—O14	100.83(19)	Mo4—O18—Mo3	124.92(19)
O24—Mo3—O14	99.65(18)	Mo4—O19—Mo7	129.98(19)
O28—Mo3—O35	100.54(18)	Mo4—O19—Mo9	123.20(19)
O24—Mo3—O35	94.49(18)	Mo7—O19—Mo9	89.55(13)
O14—Mo3—O35	150.71(16)	Mo4—O20—Mo11	147.3(2)
O28—Mo3—O17	166.81(17)	Mo4—O20—Mo10	123.09(19)
O24—Mo3—O17	89.35(16)	Mo11—O20—Mo10	89.59(13)
O14—Mo3—O17	74.50(15)	Mo9—O21—Mo7	121.1(2)
O35—Mo3—O17	80.18(15)	Mo2—O29—Mo11	126.2(2)
O28—Mo3—O18	89.53(17)	Mo9—O30—Mo10	121.2(2)
O24—Mo3—O18	166.40(16)	Mo11—O31—Mo10	121.6(2)
O14—Mo3—O18	80.74(15)	Mo8—O32—Mo11	144.0(2)
O35—Mo3—O18	79.64(15)	Mo8—O35—Mo3	139.0(2)
O17—Mo3—O18	77.60(13)	O36—Mo11—O38	104.0(2)
O34—Mo4—O18	109.1(2)	O36—Mo11—O31	100.97(19)
O34—Mo4—O19	108.7(2)	O38—Mo11—O31	100.8(2)
O18—Mo4—O19	109.83(17)	O36—Mo11—O32	92.51(19)
O34—Mo4—O20	108.7(2)	O38—Mo11—O32	100.6(2)
O18—Mo4—O20	108.54(18)	O31—Mo11—O32	151.03(17)
O19—Mo4—O20	111.87(18)	O36—Mo11—O29	167.4(2)

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O1—Mo5—O2	104.6(2)	O38—Mo11—O29	87.45(18)
O1—Mo5—O12	101.81(19)	O31—Mo11—O29	81.70(15)
O2—Mo5—O12	100.62(19)	O32—Mo11—O29	79.98(16)
O1—Mo5—O3	163.37(17)	O36—Mo11—O20	92.8(2)
O2—Mo5—O3	89.76(18)	O38—Mo11—O20	163.04(18)
O12—Mo5—O3	83.26(15)	O31—Mo11—O20	73.40(15)
O1—Mo5—O11	94.90(17)	O32—Mo11—O20	80.50(16)
O2—Mo5—O11	160.39(18)	O29—Mo11—O20	76.02(14)
O12—Mo5—O11	76.64(14)	O8—Mo12—O9	105.1(2)
O3—Mo5—O11	70.65(12)	O8—Mo12—O12	98.0(2)
O7—Mo6—O6	104.5(2)	O9—Mo12—O12	101.8(2)
O7—Mo6—O10	102.16(19)	O8—Mo12—O10	98.2(2)
O6—Mo6—O10	99.56(19)	O9—Mo12—O10	105.0(2)
O7—Mo6—O11	96.38(18)	O12—Mo12—O10	143.76(16)
O6—Mo6—O11	158.86(17)	O8—Mo12—O13	164.37(18)
O10—Mo6—O11	78.71(15)	O9—Mo12—O13	90.53(18)
O7—Mo6—O5	165.79(17)	O12—Mo12—O13	78.21(15)
O6—Mo6—O5	86.22(17)	O10—Mo12—O13	77.56(15)
O10—Mo6—O5	84.83(15)	O8—Mo12—O11	95.39(18)
O11—Mo6—O5	72.64(13)	O9—Mo12—O11	159.45(17)
O27—Mo7—O16	105.5(2)	O12—Mo12—O11	73.22(14)
O27—Mo7—O21	102.08(19)	O10—Mo12—O11	73.12(14)
O16—Mo7—O21	97.95(18)	O13—Mo12—O11	68.99(12)
O27—Mo7—O14	97.87(18)	O30—Mo9—O19	77.50(15)
O16—Mo7—O14	100.61(18)	O21—Mo9—O19	71.31(14)
O21—Mo7—O14	147.92(16)	O26—Mo9—O15	87.96(18)
O27—Mo7—O19	94.75(18)	O22—Mo9—O15	167.72(17)
O16—Mo7—O19	159.46(18)	O30—Mo9—O15	71.43(15)
O21—Mo7—O19	74.00(14)	O21—Mo9—O15	77.85(15)

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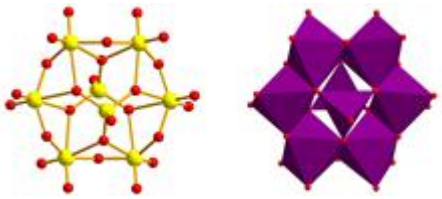
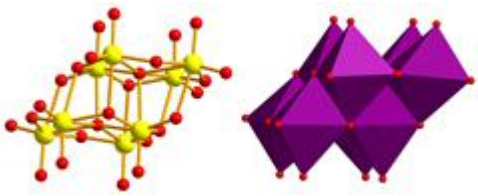
O14—Mo7—O19	79.58(14)	O19—Mo9—O15	82.40(13)
O27—Mo7—O17	164.30(17)	O39—Mo10—O33	105.3(2)
O16—Mo7—O17	88.57(17)	O39—Mo10—O31	100.8(2)
O21—Mo7—O17	82.38(15)	O33—Mo10—O31	100.66(19)
O14—Mo7—O17	72.22(14)	O39—Mo10—O30	100.1(2)
O19—Mo7—O17	71.82(13)	O33—Mo10—O30	96.90(19)
O23—Mo8—O37	106.5(2)	O31—Mo10—O30	147.93(15)
O23—Mo8—O32	109.7(2)	O39—Mo10—O15	92.23(18)
O37—Mo8—O32	107.6(2)	O33—Mo10—O15	161.24(18)
O23—Mo8—O35	108.1(2)	O31—Mo10—O15	82.07(15)
O37—Mo8—O35	110.1(2)	O30—Mo10—O15	73.08(15)
O32—Mo8—O35	114.56(17)	O39—Mo10—O20	162.51(18)
O26—Mo9—O22	103.5(2)	O33—Mo10—O20	91.72(18)
O26—Mo9—O30	105.13(19)	O31—Mo10—O20	71.61(15)
O22—Mo9—O30	100.90(18)	O30—Mo10—O20	81.30(15)
O26—Mo9—O21	100.85(18)	O15—Mo10—O20	71.38(13)
O22—Mo9—O21	103.78(19)	O26—Mo9—O19	168.65(18)
O30—Mo9—O21	138.52(16)	O22—Mo9—O19	86.60(17)

Table S2 Polyhedral components of the octamolybdate isomers

Isomers	Polyhedra	Graphical representation	Refs
α-$Mo_8O_{26}^{4-}$	6 octahedra, 2 tetrahedra		14
β-$Mo_8O_{26}^{4-}$	8 octahedra		15,16,17

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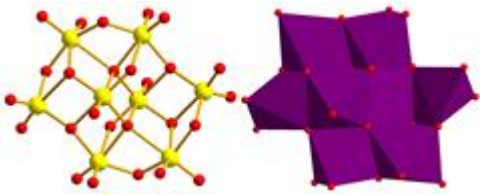
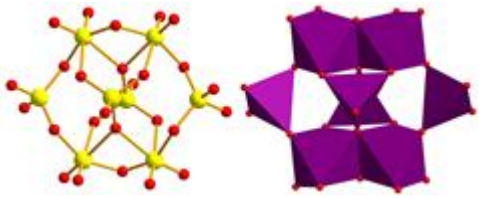
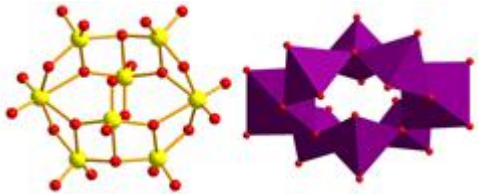
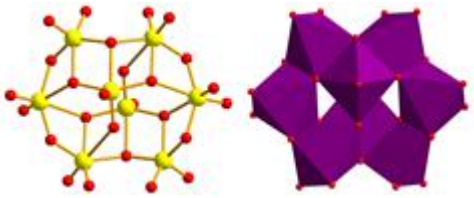
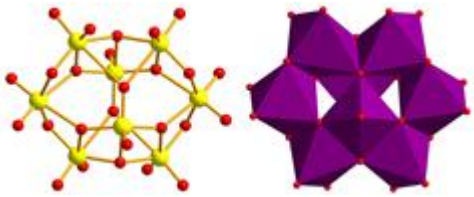
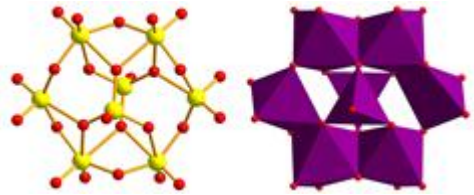
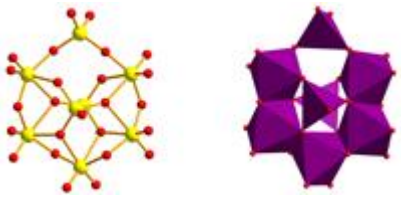
γ-$Mo_8O_{26}^{4-}$	6 octahedra, 2 square pyramids (Type A)		14,18,19
δ-$Mo_8O_{26}^{4-}$	4 octahedra, 4 tetrahedra		20,21
ε-$Mo_8O_{26}^{4-}$	6 square pyramids, 2 octahedra		21
ζ-$Mo_8O_{26}^{4-}$	4 octahedra, 4 square pyramids		22
η-$Mo_8O_{26}^{4-}$	6 octahedral, 2 square pyramids (Type B)		5, 23
θ-$Mo_8O_{26}^{4-}$	4 octahedra, 2 square pyramids, 2 tetrahedra		6
ι-$Mo_8O_{26}^{4-}$	5 octahedra, 3 tetrahedra		This paper