

Supporting Information

Two Molybdenyl Carbonates with Different Dimensional Structure Exhibiting Huge Difference in Band Gaps

Yunqiao Guo,^{‡ a} Yalan Deng,^{‡ a} Ting Zheng,^a Ling Huang,^{* a} Daojiang Gao,^a Jian Bi^a and Guohong Zou^{* b}

^a College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610068, P. R. China.

^b College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China.

E-mail: huangl026@sina.com; zough@scu.edu.cn

[‡] These authors contributed equally to this work.

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Section S1. Instruments and Computational Details

Single crystal structure determination

Single crystal X-ray diffraction data of $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$ were collected on a Bruker D8 Venture diffractometer with graphite monochromatic Mo $K\alpha$ radiation at 150(2) K. The structures were solved by the direct methods and refined with SHELX-2014.¹ The position of the heavy atoms is determined by the heavy atom method, and all the hydrogen atoms were located geometrically or in a difference Fourier map. Both of the structures were verified with PLATON.² Relevant crystallographic data for $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$ are summarized in Table 1. Further information including atomic coordinates and isotropic displacement coefficients, selected bond lengths are listed in Tables S1-S4 in the supporting information.

Powder X-ray Diffraction

X-ray diffraction were used to confirm the purity of the compounds, and polycrystalline materials were measured at room temperature on a Smart lab powder X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda=1.540598 \text{ \AA}$). The crystal samples were ground into powder suitable for diffraction experiments, and then the sample powder was put into a test piece with a very flat surface. The angular range of 2θ is from 5 to 70° , and the scan step width is 0.08° and step time is 0.2 s.

Infrared Spectroscopy

IR spectra were collected using a Vertex 70 Fourier transform infrared (FT-IR) spectrometer in the range of $4000\text{-}400 \text{ cm}^{-1}$. 1 mg powder samples of title compounds and dry KBr about 100 mg were mixed evenly in an agate mortar. After thorough grinding, the mixture was placed evenly between the solid tablet mold, then pressed and hold for 1-2 minutes under a pressure of about 10 T/cm^2 , and a uniform translucent tablet with a diameter of 13 mm and a thickness of about 1 mm was obtained.

Thermal Analysis

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC. A 10 mg crystal samples were sealed in a platinum crucible and heated from room temperature to 800° C at a rate

of 10 °C/min in a N₂ atmosphere.

UV-vis Diffuse Reflectance Spectroscopy

UV-vis diffuse reflectance spectra of Cs₂MoO₃(CO₃) and Cs₃MoO₄(HCO₃) were recorded at room temperature with a PerkinElmer Lambda-950 UV/VIS/NIR spectrophotometer and scanned in the range of 190-800 nm.

Theoretical Calculations

In order to better understand the electronic structures of Cs₂MoO₃(CO₃) and Cs₃MoO₄(HCO₃), the theoretical calculations were processed using density functional theory (DFT) in the CASTEP program suite.³ All calculations were performed using the Perdew-Burke-Ernzerhof (PBE) under generalized gradient approximation (GGA).⁴ The energy cutoffs of the plane wave basis and the *k*-point sampling Brillouin zones for Cs₂MoO₃(CO₃) and Cs₃MoO₄(HCO₃) were set to be 750 eV / 830 eV, 1 × 1 × 1 / 2 × 4 × 2, respectively.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), and calculated Bond Valence Sum for $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$	BVS
Cs1	6665(1)	2500	3145(1)	22(1)	1.126
Cs2	6641(1)	2500	10193(1)	25(1)	0.934
Mo1	5288(1)	2500	7594(1)	17(1)	5.920
O1	6285(4)	4212(5)	6403(2)	23(1)	1.962
O2	5346(4)	4671(6)	8326(2)	22(1)	2.158
O3	3221(6)	2500	7157(4)	22(1)	1.994
O4	7447(6)	2500	5179(3)	27(1)	1.973
C1	6705(8)	2500	5951(5)	21(1)	3.932

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$), and calculated Bond Valence Sum for $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$. $U_{(\text{eq})}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$	BVS
C1	3260 (9)	3050 (3)	4293 (8)	14 (4)	4.652
C2	4242 (9)	8010 (3)	5720 (8)	18 (4)	4.669
Cs1	3751.7 (11)	2851 (2)	6400.2 (17)	14.1 (4)	0.894
Cs2	2903.2 (14)	7686 (2)	7742.4 (13)	12.6 (5)	1.204
Cs3	5219 (15)	2533.6 (15)	4602.9 (18)	13.1 (5)	0.944
Cs4	7267.4 (15)	7362 (2)	5402 (17)	13.8 (5)	0.790
Cs5	8734.9 (11)	7141 (2)	3600.5 (17)	15.1 (4)	0.845
Cs6	4597.4 (15)	12624.1 (18)	2258.7 (13)	12.6 (5)	1.024
Mo1	1467.2 (19)	2687 (3)	6420.1 (19)	8.1 (6)	5.691
Mo2	6024 (2)	7554 (2)	3583 (2)	10 (6)	6.195
O1	441 (12)	2820 (3)	6498 (14)	24 (4)	1.841
O2	1730 (18)	2670 (2)	5490 (2)	25 (6)	1.833
O3	1813 (13)	380 (3)	6861 (13)	26 (5)	1.911
O4	1903 (12)	4890 (3)	6859 (13)	21 (4)	1.915
O5	5732 (13)	5310 (3)	3142 (13)	27 (5)	2.101
O6	5584 (11)	9740 (3)	3208 (12)	18 (4)	2.081
O7	7016 (11)	7880 (2)	3542 (13)	20 (4)	2.035
O8	5738 (18)	7360 (2)	4532 (19)	21 (5)	1.655
O9	3643 (11)	2810 (2)	3734 (9)	17 (4)	2.174
O10	2679 (7)	1950 (2)	4367 (9)	16 (3)	1.786
O11	3434 (8)	4278 (18)	4781 (7)	16 (3)	2.052
O12	4068 (8)	9241 (19)	5235 (7)	19 (3)	2.069
O13	4827 (7)	6920 (2)	5669 (8)	16 (3)	1.821
O14	3848 (11)	7770 (2)	6273 (10)	17 (4)	2.177
H10	2200 (6)	1800 (4)	4530 (13)	30 (7)*	1.000
H12	3610 (10)	9800 (4)	5000 (13)	70 (10)*	0.797

Table S3. Selected Bond lengths (Å) and angles (deg) for Cs₂MoO₃(CO₃).

Cs1—O1 ⁱⁱⁱ	3.222 (3)	Mo1—O1 ^{vi}	2.168 (3)
Cs1—O2 ⁱⁱⁱ	3.197 (4)	Mo1—O2	1.738 (3)
Cs1—O2 ⁱ	3.005 (4)	Mo1—O3	1.761 (5)
Cs1—O3 ^{iv}	3.2350 (7)	Mo1—O3 ^{xiii}	2.364 (5)
Cs1—O4	2.956 (5)	O1—C1	1.314 (5)
Cs2—O1 ^{vii}	3.182 (3)	O4—C1	1.246 (9)
Cs2—O2 ^{ix}	3.197 (3)	O3—Cs1 ^v	3.2349 (7)
Cs2—O2 ^{vi}	3.167 (3)	Cs2—O4 ^{xiii}	3.383 (5)
Cs2—O4 ^{vii}	3.2866 (12)	O4—Cs1—O2 ⁱ	75.47 (10)
O2—Mo1—O2 ^{vi}	106.4 (2)	O4—Cs1—O2 ⁱⁱ	75.47 (10)
O2—Mo1—O3	103.67 (15)	O4—Cs1—O2 ⁱⁱⁱ	138.12 (8)
O2—Mo1—O1 ^{vi}	149.59 (14)	O2 ⁱ —Cs1—O2 ⁱⁱⁱ	142.71 (7)
O2 ^{vi} —Mo1—O1 ^{vi}	92.97 (14)	O2 ⁱⁱ —Cs1—O2 ⁱⁱⁱ	96.38 (10)
O3—Mo1—O1 ^{vi}	93.85 (17)	O4—Cs1—O2 ^{iv}	138.12 (8)
O1 ^{vi} —Mo1—O1	60.80 (18)	O2 ⁱⁱ —Cs1—O2 ^{iv}	142.71 (7)
O2—Mo1—O3 ^{xiii}	83.34 (14)	O2 ⁱⁱⁱ —Cs1—O2 ^{iv}	69.09 (12)
O3—Mo1—O3 ^{xiii}	167.92 (9)	O2 ⁱ —Cs1—O1 ⁱⁱⁱ	162.95 (9)
O1 ^{vi} —Mo1—O3 ^{xiii}	75.78 (14)	O2 ⁱⁱ —Cs1—O1 ⁱⁱⁱ	99.58 (9)
O4—C1—O1 ^{vi}	123.4 (3)	O2 ⁱⁱⁱ —Cs1—O1 ⁱⁱⁱ	52.68 (9)
O1—C1—O1 ^{vi}	113.2 (6)	O2 ^{iv} —Cs1—O1 ⁱⁱⁱ	97.80 (9)
O1 ⁱⁱⁱ —Cs1—O1 ^{iv}	81.72 (12)	O4—Cs1—O1 ^{iv}	87.65 (9)
O2 ⁱ —Cs1—O3 ^v	125.93 (11)	O4—Cs1—O1 ⁱ	124.76 (9)
O2 ⁱⁱ —Cs1—O3 ^v	52.49 (11)	O2 ⁱ —Cs1—O1 ⁱ	49.66 (8)
O2 ⁱⁱⁱ —Cs1—O3 ^v	50.63 (11)	O2 ⁱⁱ —Cs1—O1 ⁱ	92.98 (8)
O1 ^{iv} —Cs1—O3 ^v	134.04 (10)	O2 ⁱⁱⁱ —Cs1—O1 ⁱ	96.26 (8)
O4—Cs1—O3 ^{iv}	97.10 (9)	O2 ^{iv} —Cs1—O1 ⁱ	56.77 (8)
O2 ⁱ —Cs1—O3 ^{iv}	52.49 (11)	O1 ⁱⁱⁱ —Cs1—O1 ⁱ	147.38 (6)
O2 ⁱⁱ —Cs1—O3 ^{iv}	125.93 (11)	O1 ^{iv} —Cs1—O1 ⁱ	94.83 (9)
O2 ⁱⁱⁱ —Cs1—O3 ^{iv}	119.30 (11)	O3 ^v —Cs1—O1 ⁱ	118.11 (10)
O1 ⁱⁱⁱ —Cs1—O3 ^{iv}	134.04 (10)	O3 ^{iv} —Cs1—O1 ⁱ	47.41 (10)

Symmetry codes: (i) $-x+3/2, -y+1, z-1/2$; (ii) $-x+3/2, y-1/2, z-1/2$; (iii) $-x+1, y-1/2, -z+1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+1, -y, -z+1$; (vi) $x, -y+1/2, z$; (vii) $-x+3/2, -y+1, z+1/2$; (viii) $-x+3/2, y-1/2, z+1/2$; (ix) $-x+1, -y+1, -z+2$; (x) $-x+1, y-1/2, -z+2$; (xi) $-x+3/2, -y, z+1/2$; (xii) $x-1/2, y, -z+3/2$; (xiii) $x+1/2, y, -z+3/2$; (xiv) $-x+3/2, -y, z-1/2$.

Table S4. Selected Bond lengths (Å) and angles (deg) for Cs₃MoO₄(HCO₃).

C1—O9	1.224 (7)	C2—O12	1.225 (7)
C1—O10	1.231 (7)	C2—O13	1.231 (7)
C1—O11	1.226 (7)	C2—O14	1.226 (7)
Mo1—O1	1.77 (2)	Mo2—O5	1.724 (19)
Mo1—O2	1.76 (4)	Mo2—O6	1.733 (19)
Mo1—O3	1.785 (19)	Mo2—O7	1.72 (2)
Mo1—O4	1.792 (19)	Mo2—O8	1.81 (3)
Cs1—O1 ^{vi}	2.95 (2)	Cs2—O3 ^v	3.02 (2)
Cs1—O4	3.54 (2)	Cs2—O4	2.962 (19)
Cs1—O5 ^x	3.51 (2)	Cs2—O5 ^x	3.12 (2)
Cs1—O11	3.145 (13)	Cs2—O6 ^{iv}	3.198 (19)
Cs1—O12 ^{xiv}	3.191 (13)	Cs2—O7 ^{iv}	3.201 (17)
Cs1—O13	3.464 (15)	Cs2—O9 ^{ix}	3.22 (2)
Cs1—O14 ^{xiv}	3.267 (15)	Cs2—O10 ^{ix}	3.169 (16)
Cs1—O14	3.168 (15)	Cs2—O14	3.140 (14)
Cs3—O1 ^{vi}	3.49 (3)	Cs4—O2 ^{vii}	3.321 (16)
Cs3—O2 ^{vi}	3.07 (4)	Cs4—O2 ^{vi}	3.359 (17)
Cs3—O5	3.33 (2)	Cs4—O3 ^{vi}	3.29 (2)
Cs3—O6 ^{xiv}	3.18 (2)	Cs4—O4 ^{vii}	3.25 (2)
Cs3—O8	3.222 (16)	Cs4—O7	3.44 (2)
Cs3—O8 ^{xiv}	3.438 (15)	Cs4—O8	3.08 (3)
Cs3—O9	3.15 (2)	Cs4—O10 ^{vi}	3.423 (14)
Cs3—O11	3.286 (13)	Cs4—O11 ^{vii}	3.156 (13)
Cs3—O12 ^{xiv}	3.117 (14)	Cs4—O12 ^{vii}	3.280 (15)
Cs3—O13	3.484 (14)	Cs4—O14 ^{vii}	3.15 (2)
Cs5—O4 ^{viii}	3.61 (2)	Cs6—O1 ^{xiii}	3.611 (19)
Cs5—O6 ^{vii}	3.480 (18)	Cs6—O3 ^{xiii}	3.09 (2)
Cs5—O7	2.999 (19)	Cs6—O4 ^{xii}	3.20 (2)
Cs5—O9 ^{vi}	3.189 (15)	Cs6—O6	3.053 (19)
Cs5—O9 ^{vii}	3.247 (15)	O2—Mo1—O1	109.5 (14)
Cs5—O9 ^{vii}	3.247 (15)	O14—C2—O13	116.4 (14)
Cs5—O11 ^{vii}	3.191 (13)	O9—C1—O10	117.2 (14)

Symmetry codes: (i) $x-1/2, -y+3/2, z$; (ii) $-x+1/2, y-1/2, z-1/2$; (iii) $x-1/2, -y+1/2, z$; (iv) $x+1/2, -y+3/2, z$; (v) $-x+1, -y+2, z+1/2$; (vi) $x+1/2, -y+1/2, z$; (vii) $-x+1, -y+1, z-1/2$; (viii) $x, y+1, z$; (ix) $-x+1, -y+1, z+1/2$; (x) $-x+1/2, y+1/2, z+1/2$; (xi) $-x+1, -y+2, z-1/2$; (xii) $-x+1/2, y+3/2, z-1/2$; (xiii) $-x+1/2, y+1/2, z-1/2$; (xiv) $-x+1/2, y-1/2, z+1/2$; (xv) $x, y-1, z$; (xvi) $-x+1/2, y-3/2, z+1/2$

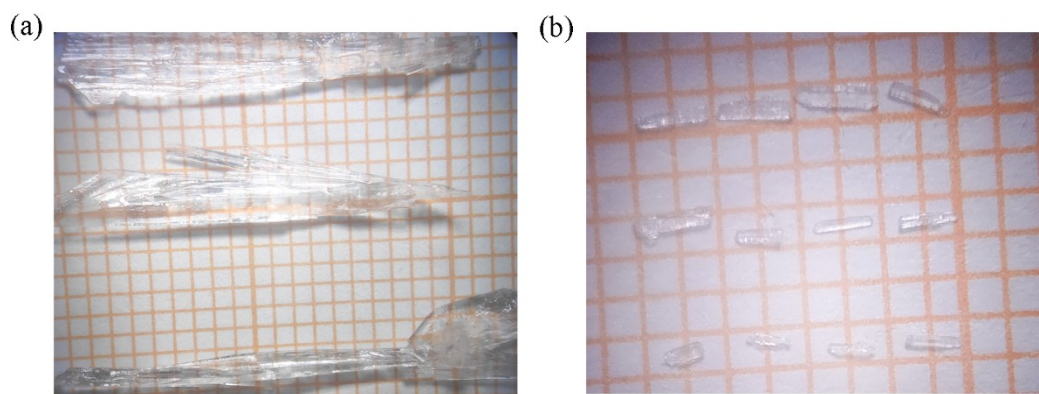


Fig. S1 The crystal photographs of (a) $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and (b) $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$.

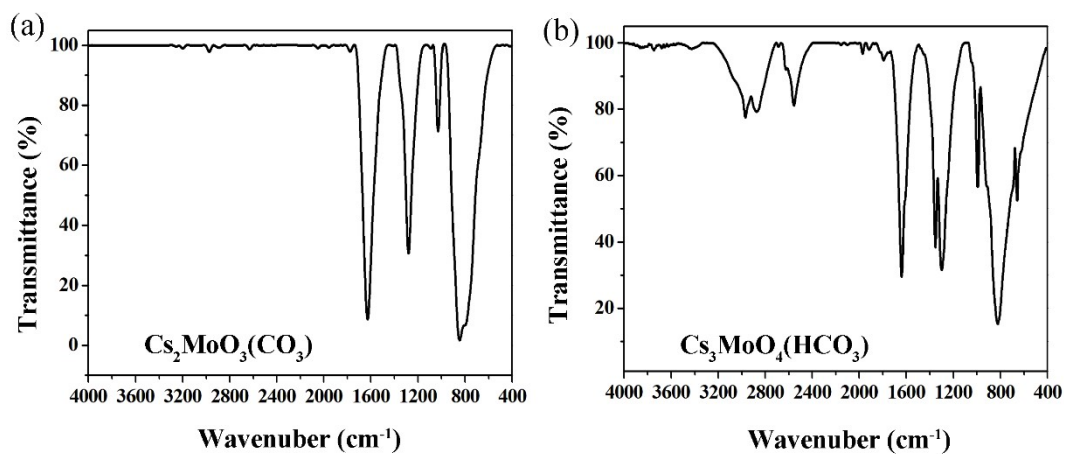


Fig. S2 The IR spectra of compounds (a) $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and (b) $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$.

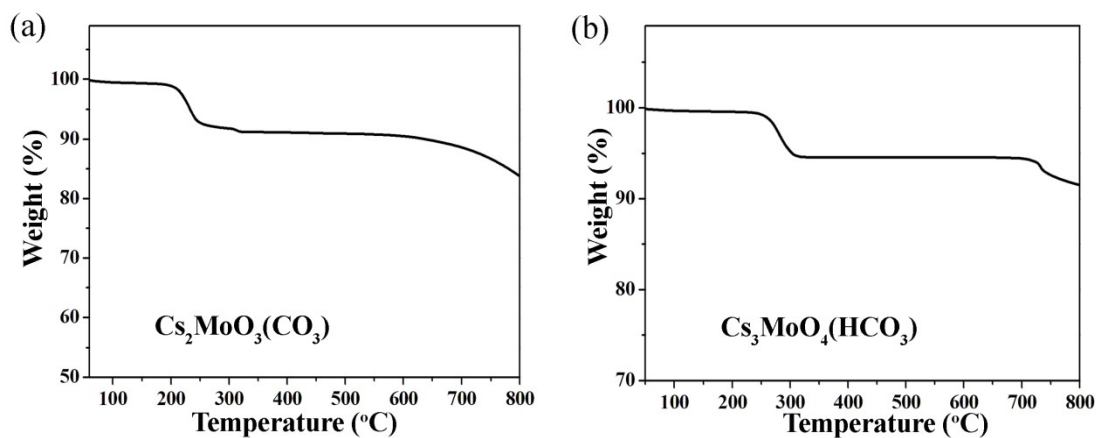


Fig. S3 TGA curves of compounds (a) $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and (b) $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$ under N_2 atmosphere.

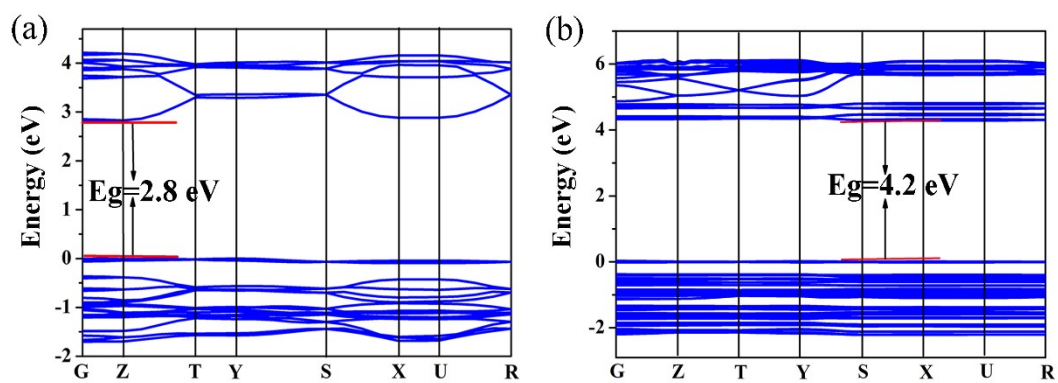


Fig. S4 Calculated band structure of (a) $\text{Cs}_2\text{MoO}_3(\text{CO}_3)$ and (b) $\text{Cs}_3\text{MoO}_4(\text{HCO}_3)$.

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