

SUPPORTING INFORMATION

Geometric Structures, Structural Evolution, and Magnetic Properties of Hybrid Chromium Maganese Oxide Clusters

Le Nhan Pham*

E-mail: lenhanhoaqn@gmail.com

Table S1: Relative energies (in eV) of the low energy isomers of CrMnO_3^+ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
^5A	A	C_1	0.00	0.00	0.01
^3A	A	C_1	0.04	0.07	0.00
^7A	A	C_1	0.05	0.01	0.06
^3A	B	C_1	0.92	1.36	0.81
^7A	C	C_1	1.17	1.45	1.17

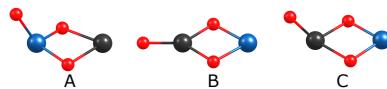


Figure S1: Geometrical structures of the lowest energy isomers of CrMnO_3^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S2: Relative energies (in eV) of the low energy isomers of CrMnO_4^+ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
^5A	A	C_1	0.00	0.00	0.00
^7A	A	C_1	1.17	0.72	1.17
^3A	B	C_1	0.66	0.88	0.66
^5A	B	C_1	0.68	0.86	0.68
^3A	C	C_1	0.67	0.85	0.67

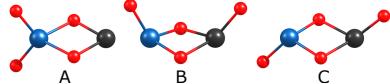


Figure S2: Geometrical structures of the lowest energy isomers of CrMnO_4^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S3: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_2\text{O}_5^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
⁴ A	A	C ₁	0.00	0.00	0.03
² A	A	C ₁	0.07	0.44	0.12
⁸ A	A	C ₁	0.12	0.05	0.18
¹⁰ A	A	C ₁	0.22	0.09	0.34
² A	B	C ₁	0.16	0.12	0.00

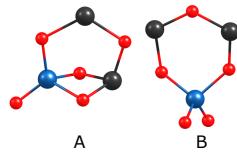


Figure S3: Geometrical structures of the lowest energy isomers of $\text{CrMn}_2\text{O}_5^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S4: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_2\text{O}_6^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
⁴ A	A	C ₁	0.00	0.00	0.00
⁶ A	A	C ₁	0.20	0.33	0.24
⁸ A	A	C ₁	0.19	0.12	0.23
⁶ A	B	C ₁	0.51	0.61	0.55
⁸ A	C	C ₁	0.45	0.45	0.30

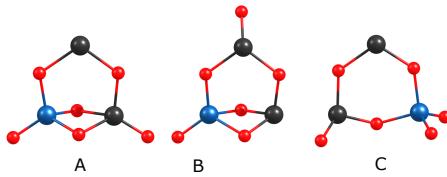


Figure S4: Geometrical structures of the lowest energy isomers of $\text{CrMn}_2\text{O}_6^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S5: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_6^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
^7A	A	C_1	0.00	0.01	0.00
^5A	A	C_1	0.00	0.00	0.03
^5A	B	C_1	0.62	0.64	0.52
^7A	B	C_1	0.63	0.64	0.52
^7A	C	C_1	0.70	0.67	0.72

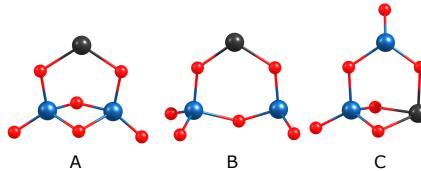


Figure S5: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{MnO}_6^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S6: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_7^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
^3A	A	C_1	0.00	0.16	0.00
^5A	A	C_1	0.09	0.28	0.09
^5A	B	C_1	0.01	0.06	0.07
^7A	B	C_1	0.76	0.48	0.86
^5A	C	C_1	0.15	0.00	0.14

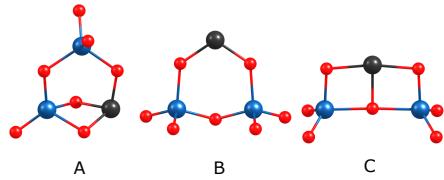


Figure S6: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{MnO}_7^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S7: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_3\text{O}_6^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
${}^3\text{A}$	A	C_1	0.00	1.62	0.05
${}^5\text{A}$	A	C_1	0.27	0.83	0.44
${}^7\text{A}$	A	C_1	0.07	0.91	0.24
${}^9\text{A}$	A	C_1	0.18	0.28	0.45
${}^{13}\text{A}$	A	C_1	0.05	0.31	0.27
${}^{13}\text{A}$	B	C_1	0.64	0.02	0.91
${}^{15}\text{A}$	B	C_1	0.63	0.00	0.90
${}^5\text{A}$	C	C_1	1.02	0.99	0.00

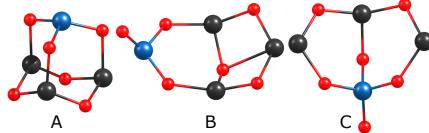


Figure S7: Geometrical structures of the lowest energy isomers of $\text{CrMn}_3\text{O}_6^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S8: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_3\text{O}_7^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
${}^3\text{A}$	A	C_1	0.00	2.49	0.00
${}^5\text{A}$	A	C_1	0.23	1.60	0.28
${}^5\text{A}$	B	C_1	1.49	0.00	1.68
${}^9\text{A}$	B	C_1	1.46	0.22	1.56

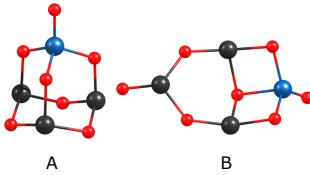


Figure S8: Geometrical structures of the lowest energy isomers of $\text{CrMn}_3\text{O}_7^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S9: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_7^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
¹⁰ A	A	C ₁	0.00	0.00	0.01
² A	B	C ₁	0.21	1.40	0.00
⁴ A	B	C ₁	0.10	0.67	0.21
⁶ A	B	C ₁	0.35	0.68	0.54

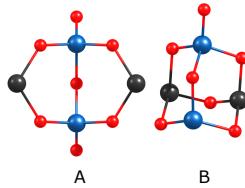


Figure S9: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_7^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S10: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_8^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
² A	A	C ₁	0.00	0.00	0.49
⁴ A	A	C ₁	0.50	1.54	0.83
⁶ A	A	C ₁	0.47	1.02	0.00
⁸ A	A	C ₁	0.47	0.38	0.15
¹⁰ A	A	C ₁	0.54	0.14	0.26
⁶ A	B	C ₁	1.64	1.34	1.18

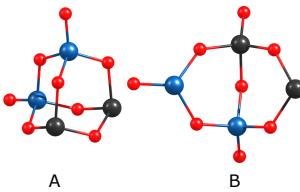


Figure S10: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_8^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S11: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_8^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
${}^3\text{A}$	A	C_1	0.00	0.00	0.00
${}^5\text{A}$	A	C_1	0.36	0.76	0.21
${}^7\text{A}$	A	C_1	0.20	0.17	0.24
${}^3\text{A}$	B	C_1	0.76	0.44	0.82
${}^5\text{A}$	B	C_1	0.92	0.47	1.08

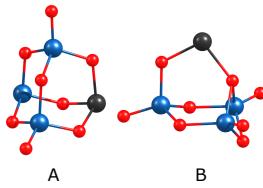


Figure S11: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_8^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S12: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_9^+$ calculated at different DFT levels

state	isomer	sym.	method		
			TPSS	B3P86	BP86
${}^5\text{A}$	A	C_1	0.00	0.00	0.13
${}^7\text{A}$	A	C_1	0.36	0.12	0.00
${}^5\text{A}$	B	C_1	1.68	1.49	1.78

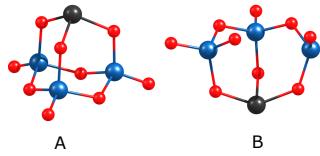


Figure S12: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_9^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S13: Relative energies (in eV) of the low energy isomer of CrMnO_2^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
⁹ A	A	C ₁	0.00
³ A	A	C ₁	0.05
⁵ A	A	C ₁	0.49
⁷ A	A	C ₁	0.59



Figure S13: The geometrical structure of the lowest energy isomer of CrMnO_2^+ . The shown structure is obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S14: Relative energies (in eV) of the low energy isomers of CrMnO_5^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^3A	A	C_1	0.00
^3A	B	C_1	0.10
^1A	C	C_1	0.28
^5A	C	C_1	1.02

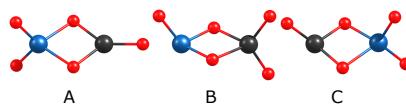


Figure S14: The geometrical structure of the lowest energy isomer of CrMnO_5^+ . The shown structure is obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S15: Relative energies (in eV) of the low energy isomer of CrMnO_6^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^1A	A	C_1	0.00
^3A	A	C_1	0.56

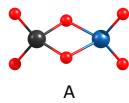


Figure S15: The geometrical structure of the lowest energy isomer of CrMnO_6^+ . The shown structure is obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S16: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_2\text{O}_4^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^6A	A	C_1	0.00
^2A	A	C_1	0.13
^8A	A	C_1	0.39
^4A	B	C_1	0.85

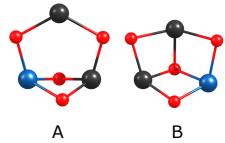


Figure S16: The geometrical structure of the lowest energy isomer of $\text{CrMn}_2\text{O}_4^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S17: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_2\text{O}_7^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^6A	A	C_1	0.00
^4A	A	C_1	0.05
^2A	B	C_1	0.30
^4A	B	C_1	0.38
^6A	B	C_1	0.41
^2A	C	C_1	0.47
^4A	C	C_1	0.48
^6A	C	C_1	0.48

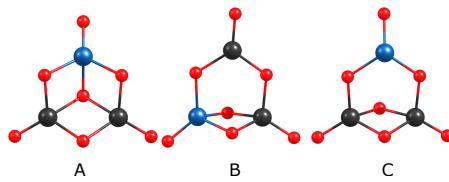


Figure S17: The geometrical structure of the lowest energy isomer of $\text{CrMn}_2\text{O}_7^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S18: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_2\text{O}_8^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^2A	A	C_1	0.00
^4A	A	C_1	0.08
^4A	B	C_1	0.53
^2A	B	C_1	0.68
^4A	C	C_1	0.81
^2A	C	C_1	0.83

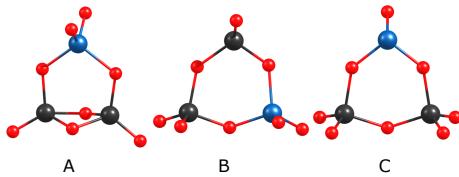


Figure S18: The geometrical structure of the lowest energy isomer of $\text{CrMn}_2\text{O}_8^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S19: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_3^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
³ A	A	C ₁	0.00
¹¹ A	B	C ₁	0.49
⁷ A	A	C ₁	0.51
¹ A	A	C ₁	0.74
⁹ A	B	C ₁	0.82

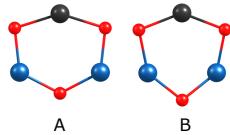


Figure S19: The geometrical structure of the lowest energy isomer of $\text{Cr}_2\text{MnO}_3^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S20: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_4^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
³ A	A	C ₁	0.00
⁵ A	A	C ₁	0.01
⁹ A	A	C ₁	0.18
⁷ A	A	C ₁	0.20
³ A	B	C ₁	0.33
¹ A	A	C ₁	0.38
⁵ A	C	C ₁	0.68
³ A	C	C ₁	0.73

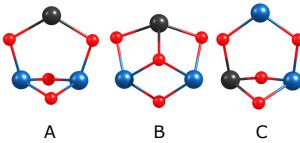


Figure S20: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{MnO}_4^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S21: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_5^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^3A	A	C_1	0.00
^7A	A	C_1	0.05
^5A	A	C_1	0.50
^5A	B	C_1	0.52
^9A	B	C_1	0.57
^7A	B	C_1	0.79
^3A	C	C_1	0.81

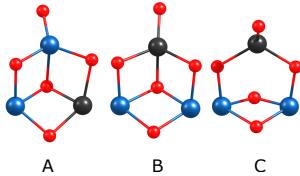


Figure S21: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{MnO}_5^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S22: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_8^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^3A	A	$\text{C}1$	0.00
^1A	A	$\text{C}1$	0.20
^3A	B	$\text{C}1$	0.28
^3A	C	$\text{C}1$	0.35
^1A	C	$\text{C}1$	0.38
^3A	D	$\text{C}1$	0.57
^1A	B	$\text{C}1$	0.63

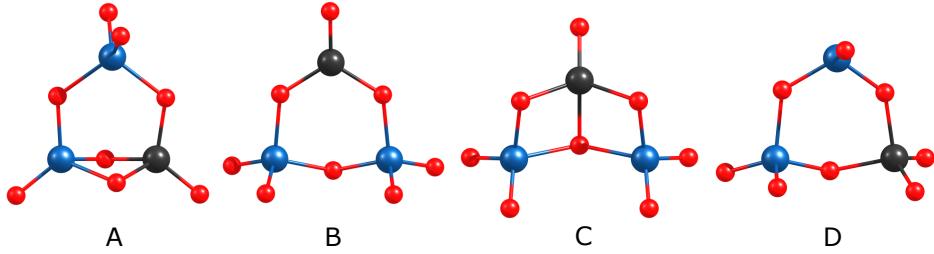


Figure S22: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{MnO}_8^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S23: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{MnO}_9^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^1A	A	C1	0.00
^3A	A	C1	0.87
^5A	A	C1	2.26

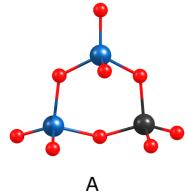


Figure S23: Geometrical structures of the lowest energy isomer of $\text{Cr}_2\text{MnO}_9^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S24: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_5^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^8A	A	C ₁	0.00
^4A	A	C ₁	0.10
^{10}A	A	C ₁	0.14
^{2}A	A	C ₁	0.20
^{6}A	A	C ₁	0.39
^{12}A	A	C ₁	0.41
^{6}A	B	C ₁	0.75
^{12}A	B	C ₁	0.77
^4A	C	C ₁	0.94
^6A	D	C ₁	0.94

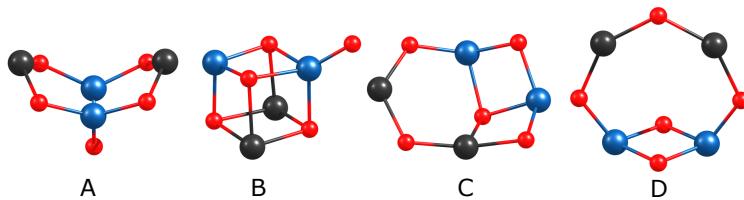


Figure S24: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_5^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S25: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_3\text{O}_5^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
⁷ A	A	C_1	0.00
¹¹ A	A	C_1	0.03
⁵ A	A	C_1	0.19
¹³ A	A	C_1	0.30
¹⁷ A	A	C_1	0.31
⁷ A	B	C_1	0.35
⁵ A	B	C_1	0.46
¹⁷ A	A	C_1	0.36
¹ A	A	C_1	0.45
³ A	A	C_1	0.47
³ A	C	C_1	0.66
¹⁵ A	B	C_1	0.69
¹¹ A	D	C_1	0.71
¹⁷ A	B	C_1	0.76

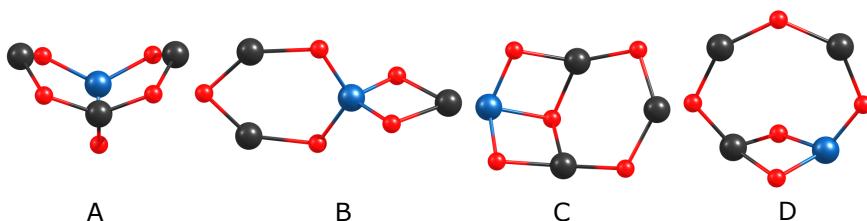


Figure S25: Geometrical structures of the lowest energy isomers of $\text{CrMn}_3\text{O}_5^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S26: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_5^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^7A	A	C_1	0.00
^9A	A	C_1	0.19
^3A	A	C_1	0.23
^3A	B	C_1	0.28
^{11}A	A	C_1	0.35
^9A	C	C_1	0.35
^9A	B	C_1	0.41
^{15}A	C	C_1	0.42
^{15}A	B	C_1	0.47
^{15}A	A	C_1	0.53
^{15}A	A	C_1	0.54
^{15}A	D	C_1	0.76

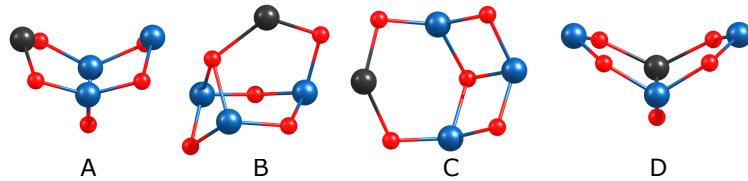


Figure S26: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_5^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S27: Relative energies (in eV) of the low energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_6^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
⁸ A	A	C ₁	0.00
⁴ A	B	C ₁	0.06
⁶ A	B	C ₁	0.12
⁸ A	B	C ₁	0.12
² A	B	C ₁	0.22
¹⁰ A	A	C ₁	0.38
¹⁰ A	B	C ₁	0.40
² A	A	C ₁	0.53
⁶ A	A	C ₁	0.62

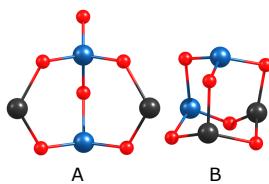


Figure S27: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_6^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S28: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_6^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
¹¹ A	A	C ₁	0.00
⁷ A	A	C ₁	0.03
⁵ A	A	C ₁	0.03
⁹ A	A	C ₁	0.05
³ A	A	C ₁	0.17
⁷ A	B	C ₁	0.90

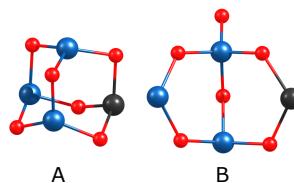


Figure S28: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_6^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S29: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_7^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^5A	A	C_1	0.00
^7A	A	C_1	0.16
^3A	A	C_1	0.17
^1A	A	C_1	0.20
^9A	A	C_1	0.21
^7A	B	C_1	0.61

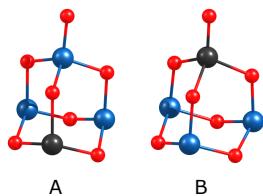


Figure S29: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_7^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S30: Relative energies (in eV) of the low energy isomers of $\text{CrMn}_3\text{O}_8^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^5A	A	C_1	0.00
^7A	A	C_1	0.06
^3A	A	C_1	0.19
^9A	A	C_1	0.45
^{11}A	A	C_1	0.60
^5A	B	C_1	0.77

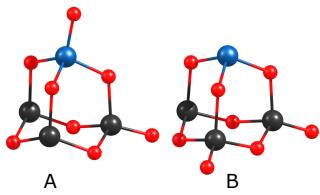


Figure S30: Geometrical structures of the lowest energy isomers of CrMn₃O₈⁺. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S31: Relative energies (in eV) of the low energy isomers of CrMn₃O₉⁺ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
³ A	A	C ₁	0.00
⁵ A	A	C ₁	0.15
⁷ A	A	C ₁	0.66
³ A	B	C ₁	1.09

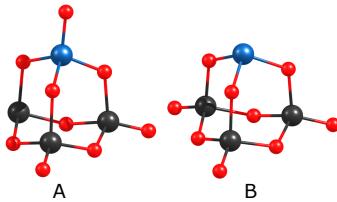


Figure S31: Geometrical structures of the lowest energy isomers of CrMn₃O₉⁺. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S32: Relative energies (in eV) of the low energy isomers of Cr₂Mn₂O₉⁺ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
⁴ A	A	C ₁	0.00
⁶ A	A	C ₁	0.51
² A	A	C ₁	0.70
⁸ A	A	C ₁	0.74
⁴ A	B	C ₁	1.14

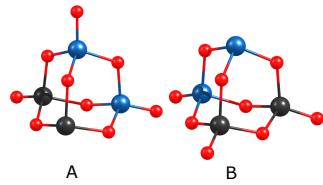


Figure S32: Geometrical structures of the lowest energy isomers of $\text{Cr}_2\text{Mn}_2\text{O}_9^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S33: Relative energies (in eV) of the low energy isomer of $\text{Cr}_3\text{MnO}_{10}^+$ calculated at the TPSS level

state	sym.	relative energy (eV)
^1A	C_1	0.00
^3A	C_1	0.48
^5A	C_1	0.92

Table S34: Relative energies (in eV) of the low energy isomer of $\text{Cr}_2\text{Mn}_2\text{O}_{10}^+$ calculated at the TPSS level

state	sym.	relative energy (eV)
^2A	C_1	0.00
^4A	C_1	0.51
^6A	C_1	1.01

Table S35: Relative energies (in eV) of the low energy isomer of $\text{CrMn}_3\text{O}_{10}^+$ calculated at the TPSS level

state	sym.	relative energy (eV)
${}^3\text{A}$	C_1	0.00
${}^1\text{A}$	C_1	0.26
${}^5\text{A}$	C_1	0.46
${}^7\text{A}$	C_1	0.93



Figure S33: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_{10}^+$, $\text{Cr}_2\text{Mn}_2\text{O}_{10}^+$, and $\text{CrMn}_3\text{O}_{10}^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S36: Relative energies (in eV) of the low energy isomers of $\text{Cr}_3\text{MnO}_{11}^+$ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
${}^3\text{A}$	A	C_1	0.00
${}^3\text{A}$	B	C_1	0.18
${}^1\text{A}$	B	C_1	0.31
${}^1\text{A}$	C	C_1	0.65
${}^3\text{A}$	D	C_1	0.91

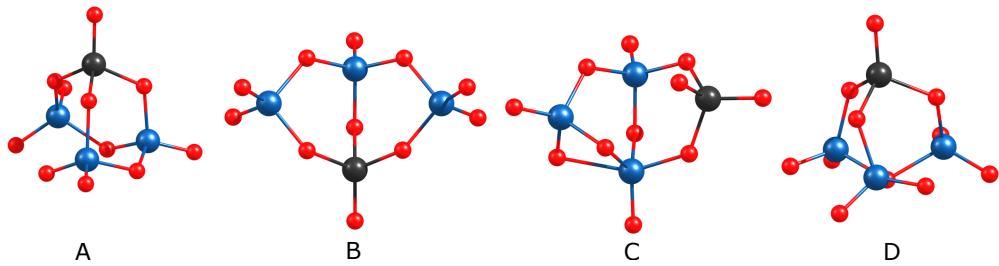


Figure S34: Geometrical structures of the lowest energy isomers of $\text{Cr}_3\text{MnO}_{11}^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium, manganese, and oxygen atoms are represented as blue, black, and red spheres, respectively.

Table S37: Relative energies (in eV) of the low energy isomers of Cr_4O_5^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
⁴ A	A	C ₁	0.00
¹⁴ A	B	C ₁	0.11
⁸ A	C	C ₁	0.12
¹⁴ A	A	C ₁	0.14
¹² A	A	C ₁	0.16
¹⁴ A	C	C ₁	0.17
⁸ A	B	C ₁	0.19
¹⁴ A	A	C ₁	0.24
⁸ A	A	C ₁	0.26
¹² A	C	C ₁	0.33
² A	A	C ₁	0.34
⁶ A	A	C ₁	0.43
¹⁰ A	C	C ₁	0.67
¹⁰ A	B	C ₁	0.72

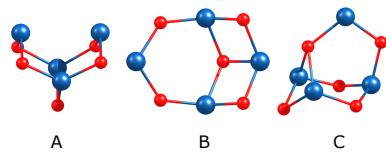


Figure S35: Geometrical structures of the lowest energy isomers of Cr_4O_5^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium and oxygen atoms are represented as blue and red spheres, respectively.

Table S38: Relative energies (in eV) of the low energy isomers of Cr_4O_6^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^{10}A	A	C_1	0.00
^6A	A	C_1	0.27
^8A	A	C_1	0.30
^{12}A	A	C_1	0.36
^{12}A	B	C_1	1.67
^2A	C	C_1	1.72

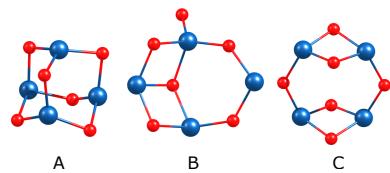


Figure S36: Geometrical structures of the lowest energy isomers of Cr_4O_6^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium and oxygen atoms are represented as blue and red spheres, respectively.

Table S39: Relative energies (in eV) of the low energy isomers of Cr_4O_7^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^{10}A	A	C_1	0.00
^4A	A	C_1	0.10
^8A	A	C_1	0.12
^6A	A	C_1	0.15
^2A	A	C_1	0.38
^{10}A	B	C_1	1.27
^{10}A	C	C_1	1.34

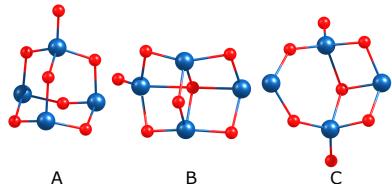


Figure S37: Geometrical structures of the lowest energy isomers of Cr_4O_7^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium and oxygen atoms are represented as blue and red spheres, respectively.

Table S40: Relative energies (in eV) of the low energy isomers of Cr_4O_8^+ calculated at the TPSS level

state	isomer	sym.	relative energy (eV)
^2A	A	C_1	0.00
^4A	A	C_1	0.19
^6A	A	C_1	0.24
^8A	A	C_1	0.47
^6A	B	C_1	1.15
^2A	C	C_1	1.16
^6A	C	C_1	1.17

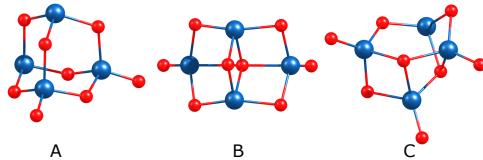


Figure S38: Geometrical structures of the lowest energy isomers of Cr_4O_8^+ . The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium and oxygen atoms are represented as blue and red spheres, respectively.

Table S41: Relative energies (in eV) of the low energy isomers of Cr_4O_9^+ calculated at the TPSS level

state	sym.	relative energy (eV)
^4A	C_1	0.00
^6A	C_1	0.07
^2A	C_1	0.58

Table S42: Relative energies (in eV) of the low energy isomers of $\text{Cr}_4\text{O}_{10}^+$ calculated at the TPSS level

state	sym.	relative energy (eV)
^2A	C_1	0.00
^4A	C_1	0.59
^6A	C_1	3.00

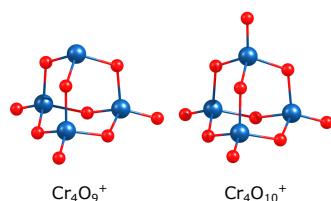


Figure S39: Geometrical structures of the lowest energy isomers of Cr_4O_9^+ and $\text{Cr}_4\text{O}_{10}^+$. The shown structures are obtained with the TPSS/def2TZVP optimizations. Chromium and oxygen atoms are represented as blue and red spheres, respectively.

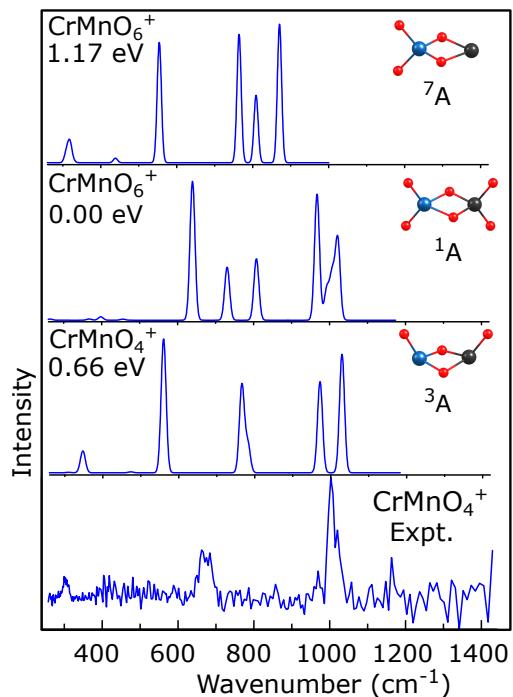


Figure S40: Experimental IRMPD and simulated harmonic IR spectra of CrMnO_4^+ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

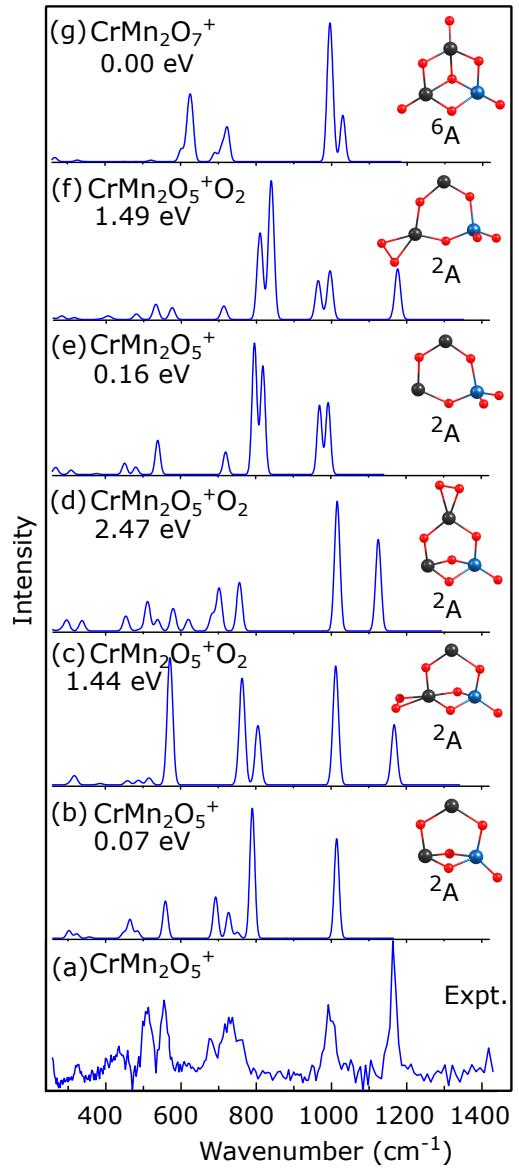


Figure S41: Experimental IRMPD and simulated harmonic IR spectra of $\text{CrMn}_2\text{O}_5^+$ and $\text{CrMn}_2\text{O}_5^+\text{O}_2$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

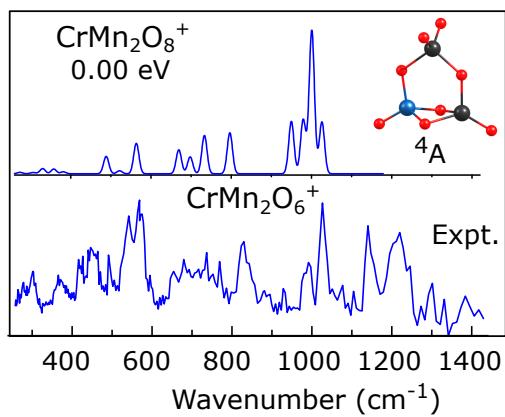


Figure S42: Experimental IRMPD and simulated harmonic IR spectra of $\text{CrMn}_2\text{O}_8^+$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

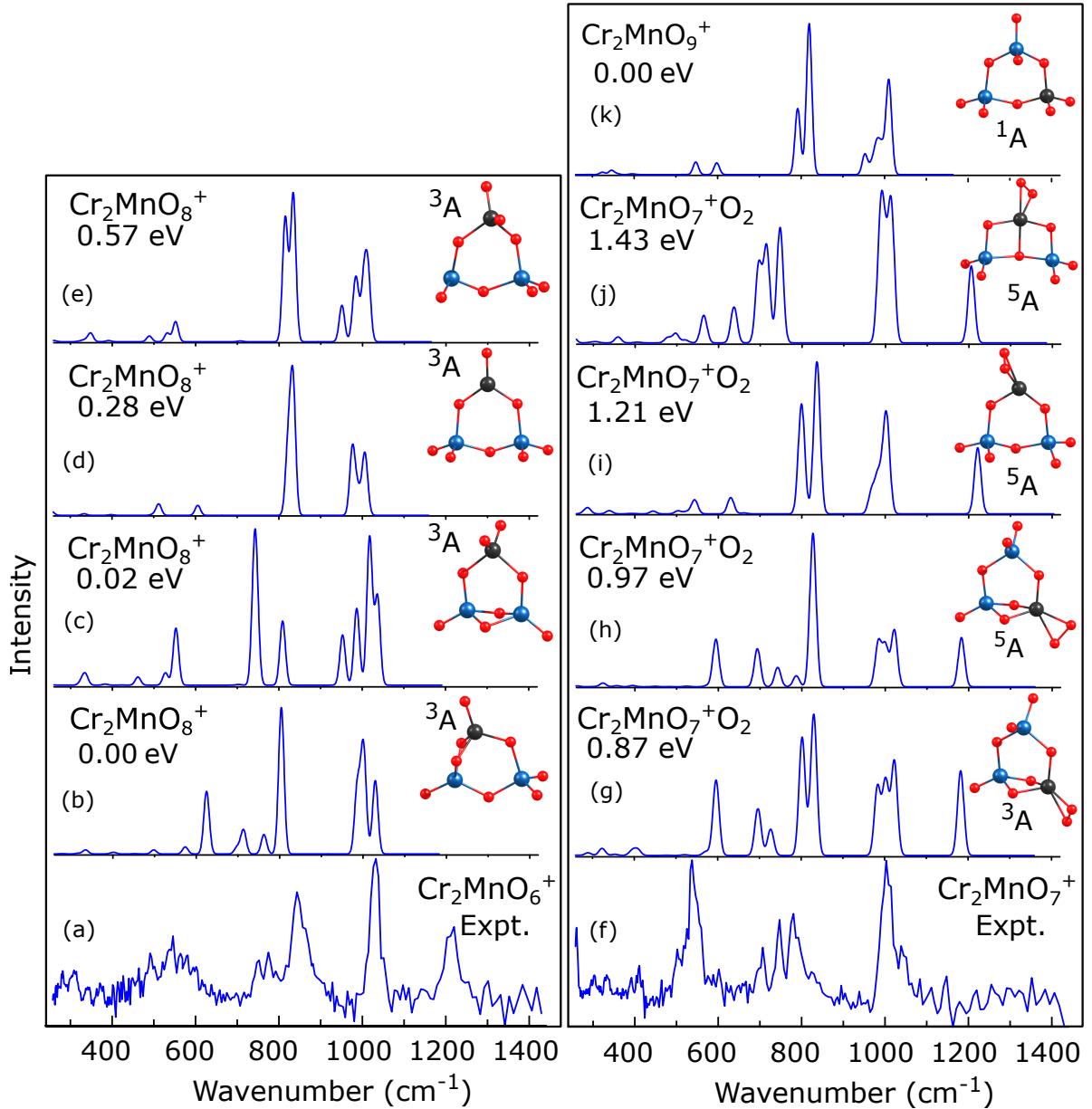


Figure S43: Experimental IRMPD and simulated harmonic IR spectra of the mother cluster $\text{Cr}_2\text{MnO}_8^+$, and $\text{Cr}_2\text{MnO}_7^+\text{O}_2$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

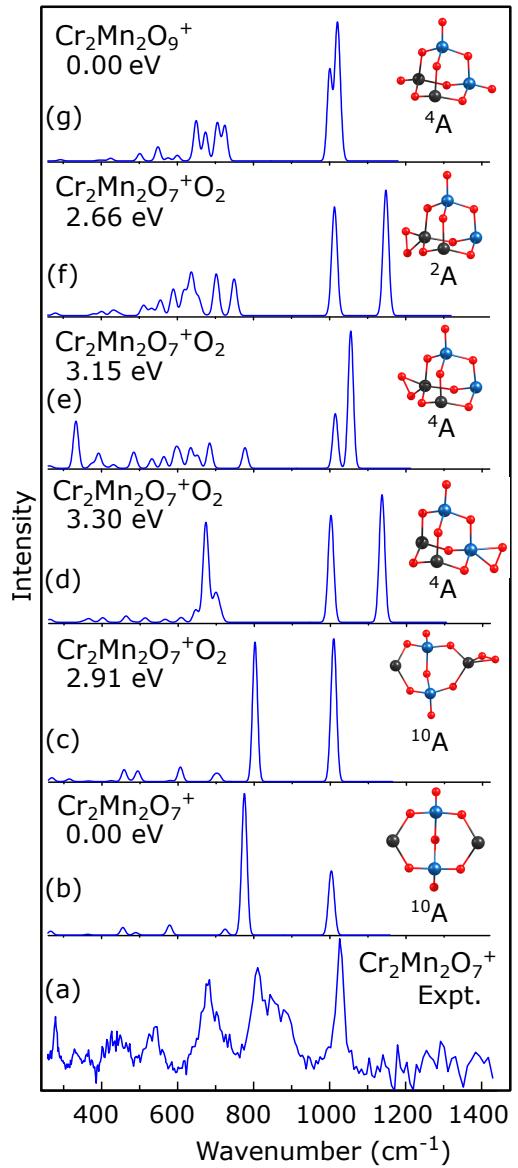


Figure S44: Experimental IRMPD and simulated harmonic IR spectra of $\text{Cr}_2\text{Mn}_2\text{O}_7^+$ and $\text{Cr}_2\text{Mn}_2\text{O}_7^+\text{O}_2$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

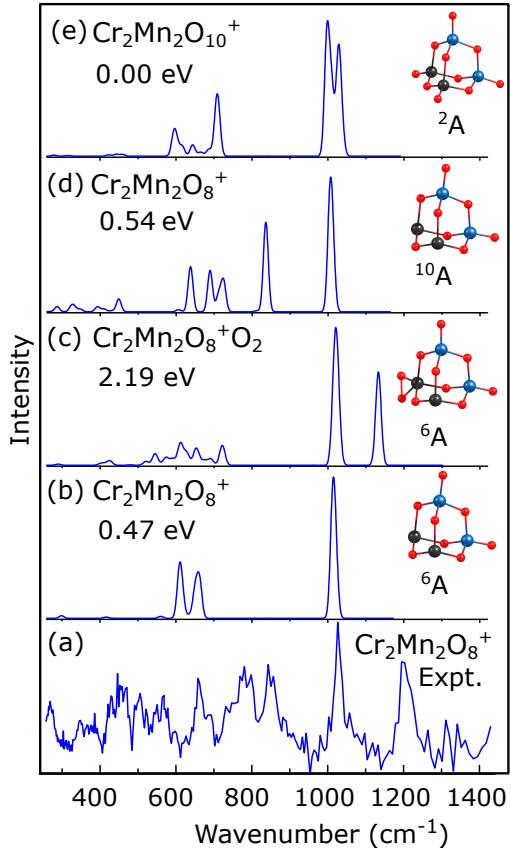


Figure S45: Experimental IRMPD and simulated harmonic IR spectra of $\text{Cr}_2\text{Mn}_2\text{O}_8^+$ and $\text{Cr}_2\text{Mn}_2\text{O}_8^+\text{O}_2$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

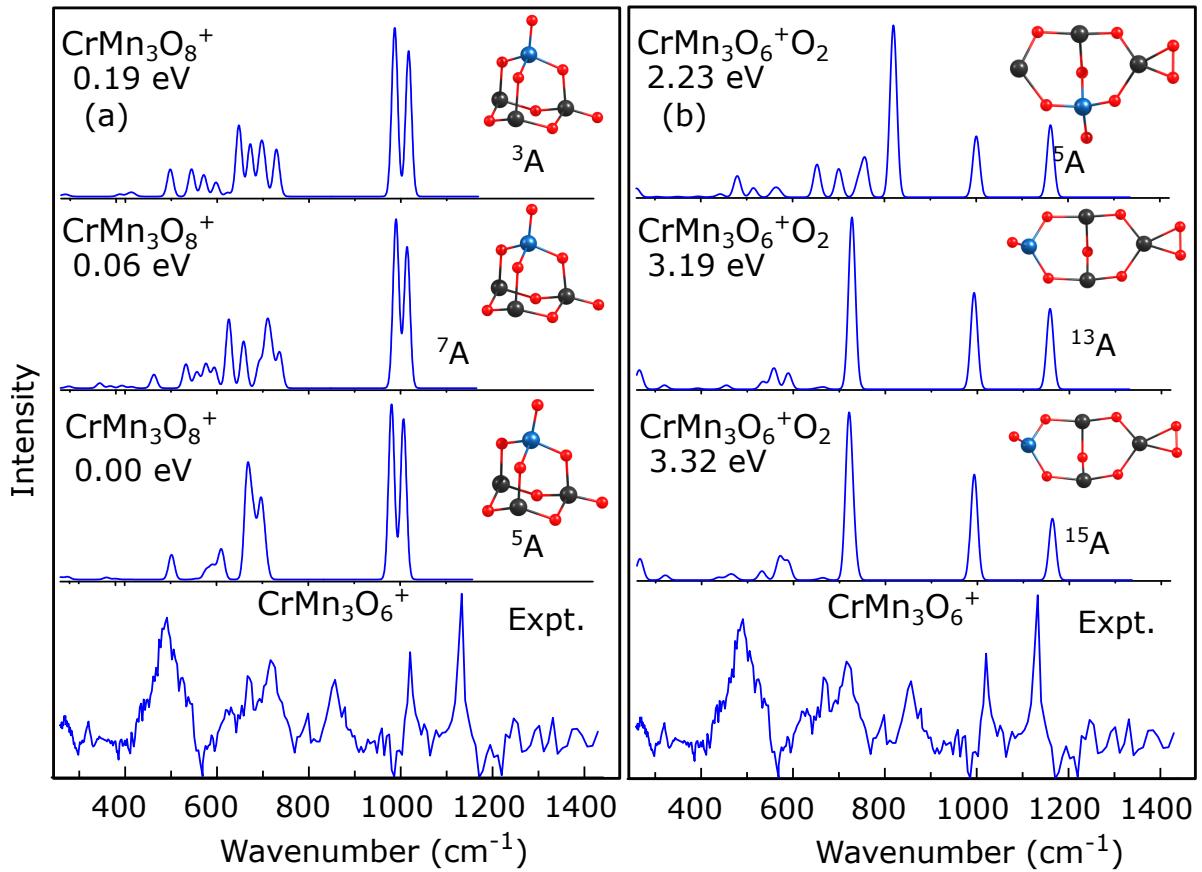


Figure S46: Experimental IRMPD and simulated harmonic IR spectra of CrMn₃O₆⁺O₂ and the mother cluster CrMn₃O₈⁺ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

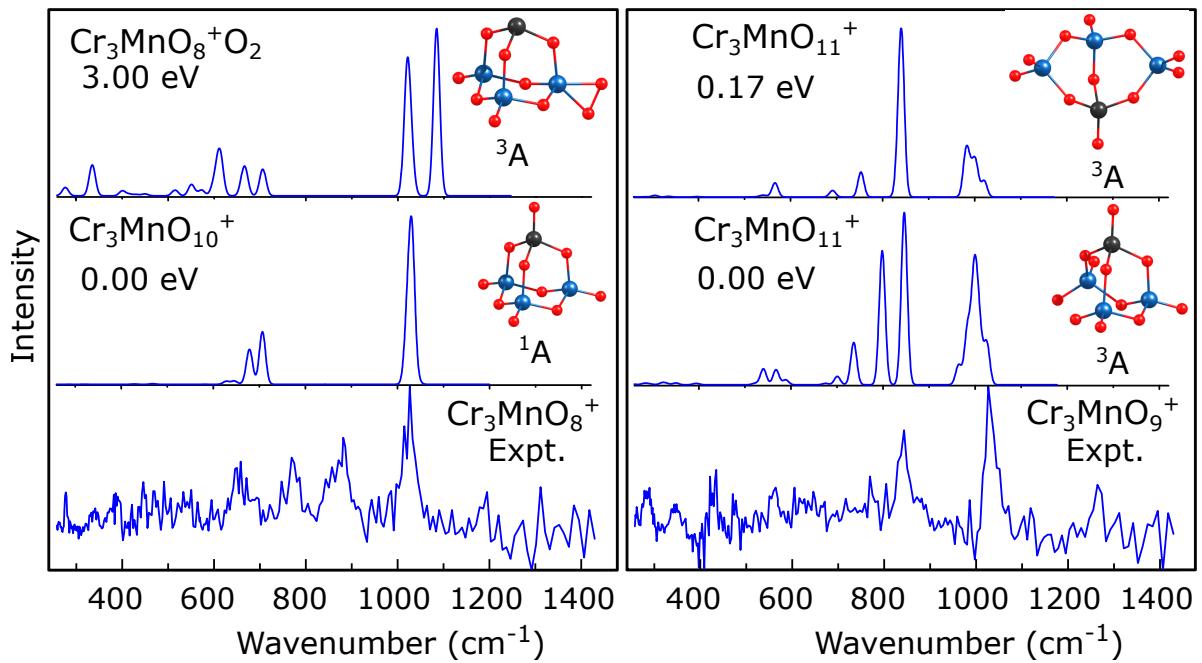


Figure S47: Experimental IRMPD and simulated harmonic IR spectra of $\text{Cr}_3\text{MnO}_8^+\text{O}_2$ and the mother cluster $\text{Cr}_3\text{MnO}_{10}$, and the mother cluster $\text{Cr}_3\text{MnO}_{11}$ at the TPSS level. The geometrical structures of selected low-lying states are given as inset with chromium (manganese) atoms represented by blue (black) balls. Relative energies are considered within the same molecular sizes.

Table S43: Local magnetic moments of metallic sites in Cr_4O_6^+ , $\text{Cr}_3\text{MnO}_6^+$, $\text{Cr}_2\text{Mn}_2\text{O}_6^+$, $\text{CrMn}_3\text{O}_6^+$

cluster	metallic site			
Cr_4O_6^+	Cr1: 2.1	Cr2: 2.9	Cr3: 2.1	Cr4: 2.1
$\text{Cr}_3\text{MnO}_6^+$	Cr1: 2.0	Cr2: 2.79	Cr3: 2.0	Mn4: 3.3
$\text{Cr}_2\text{Mn}_2\text{O}_6^+$	Cr1: -1.6	Cr2: -1.4	Mn3: 2.1	Mn4: 3.9
$\text{CrMn}_3\text{O}_6^+$	Cr1: -0.6	Mn2: 0.61	Mn3: -2.1	Mn4: 4.1