Supplementary Information (SI) for RSC Advances.

Stability and magnetic properties of transition metal (V, Cr, Mn and Fe) doped cobalt oxide clusters: A density functional theory investigation

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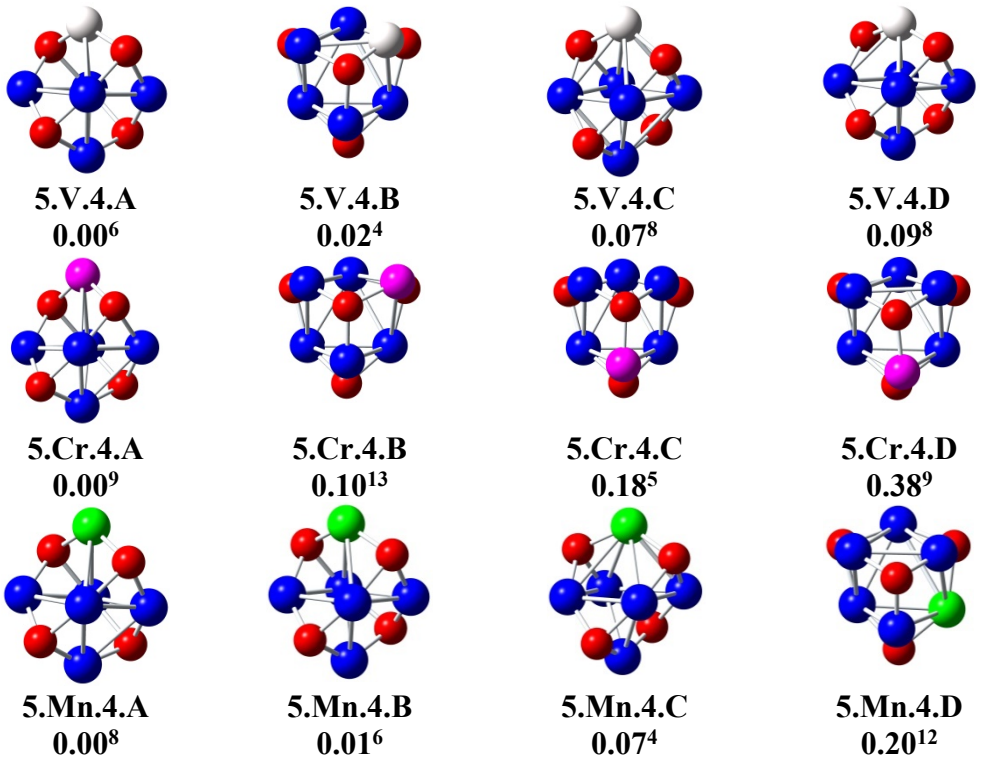
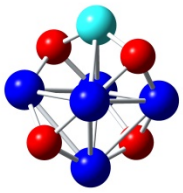
SUPPORTING INFORMATION

Figure S1. Calculated geometries of ground-state structures and stable low-lying isomers of $Co_{n-1}TMO_{n-2}^+$ clusters with (n=6-8). The values after slash indicate the spin multiplicities and the differences in total energy (in eV) from the corresponding ground states. We denote each structure as a.TM.b.x, in which a and b stands for number of Co and O atoms in cluster $Co_{n-1}TMO_{n-2}^+$ and x is labeled as A, B, C and D for isomers with increasing order of energy. The red, blue, dark gray, pink, green, and cyan spheres represent O, Co, V, Cr, Mn, and Fe atoms.





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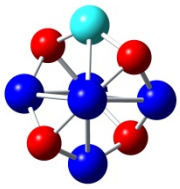

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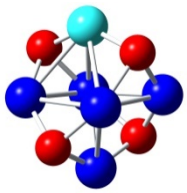

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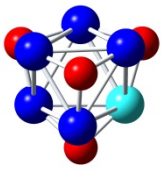

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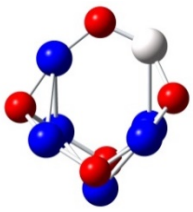

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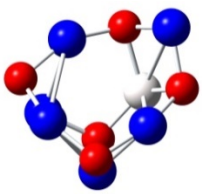

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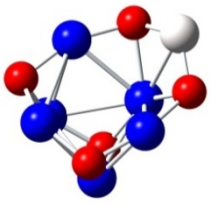

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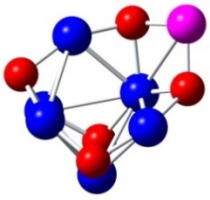

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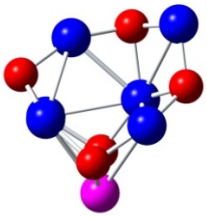

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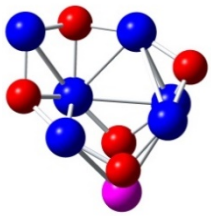

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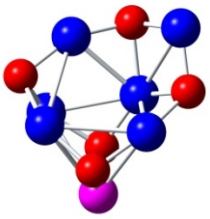

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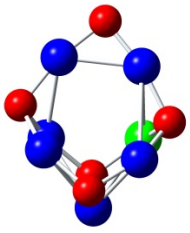

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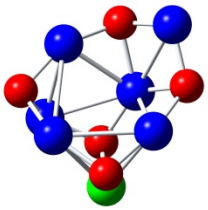

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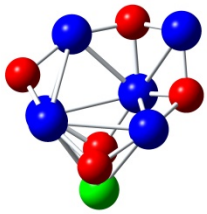

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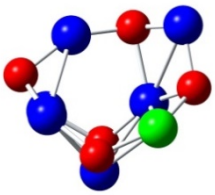

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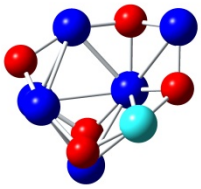

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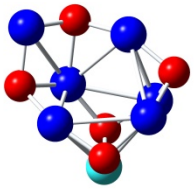

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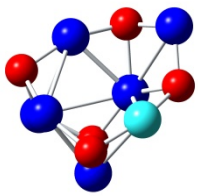

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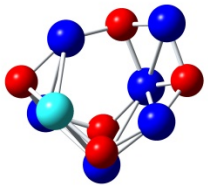

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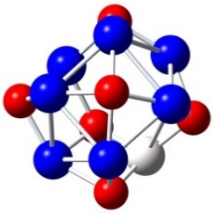

7.V.6.A
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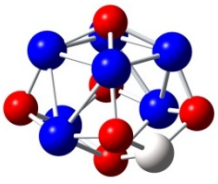

7.V.6.B
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7.V.6.C
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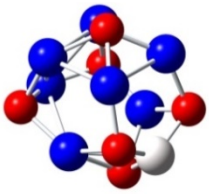

7.V.6.D
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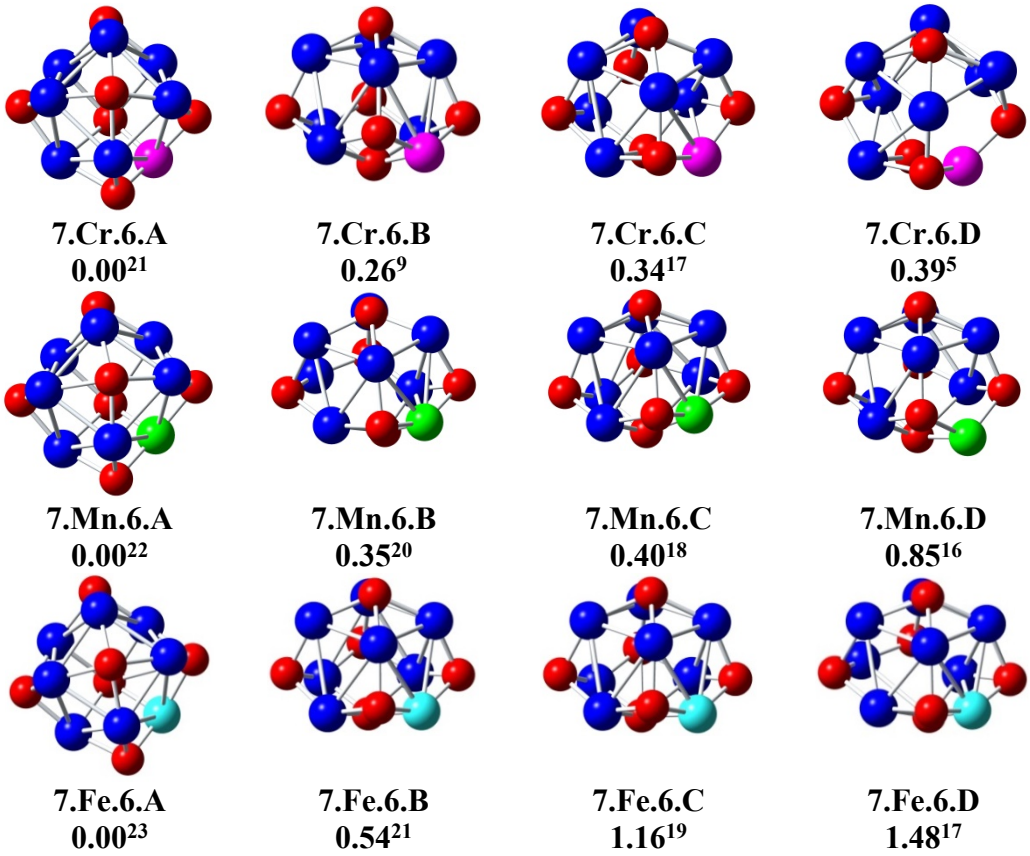

Table S1. Comparison table of different calculation functions for TM-O dimers.

Functional	Basis set	E_b (eV)				
		Co-O	V-O	Cr-O	Mn-O	Fe-O
B3LYP	6-31+G(d)	3.48	6.29	4.26	3.96	4.78
	Lanl2dz	2.90	5.74	4.06	2.87	2.62
B3P86	6-31+G(d)	4.37	7.49	3.90	2.64	4.08
	Lanl2dz	2.95	5.82	4.16	2.90	3.99
B3PW91	6-31+G(d)	3.08	6.12	3.69	2.45	2.85
	Lanl2dz	1.16	5.54	3.96	2.71	2.88
PBEPBE	6-31+G(d)	4.86	7.19	4.47	2.99	3.63
	Lanl2dz	3.03	0.75	4.71	3.28	3.60
Exp		3.98 ± 0.14 [1]	6.49 ± 0.19 [1]	4.45 ± 0.30 [1]	4.18 ± 0.43 [1]	4.05 ± 0.18 [1]

[1]. J. Shee et al. J. Chem. Theory Comput. 2019, 15, 4, 2346.

Table S2. The binding energy for Co-TM dimers.

Functional	Basis set	E_b (eV)				
		Co-Co	Co-V	Co-Cr	Co-Mn	Co-Fe
B3LYP	6-31+G(d)	1.38	1.43	1.25	0.88	1.52

Table S3. The binding energy for Co-TM dimers

Clusters	Loss TM	Loss Co	Loss O	Loss CoO
$Co_5VO_4^+$	0.002072	0.001463	0.001619	0.002474
$Co_5CrO_4^+$	0.00201	0.000504	0.001453	0.002333
$Co_5MnO_4^+$	0.002053	0.001645	0.001514	0.002461
$Co_5FeO_4^+$	0.001942	0.001458	0.001419	0.002289
$Co_6VO_5^+$	0.001468	0.001262	0.001689	0.001553
$Co_6CrO_5^+$	0.001452	0.001302	0.001641	0.001656
$Co_6MnO_5^+$	0.001408	0.00129	0.001467	0.0016
$Co_6FeO_5^+$	0.001424	0.001241	0.001416	0.001662
$Co_7VO_6^+$	0.0018	0.001437	0.001654	0.002067
$Co_7CrO_6^+$	0.001877	0.001557	0.001518	0.002105
$Co_7MnO_6^+$	0.001803	0.001433	0.001425	0.002043
$Co_7FeO_6^+$	0.001758	0.001517	0.001562	0.002046

Table S4. AOs contributions in the SOMOs of the cation $Co_6O_4^+$, $Co_7O_5^+$, and $Co_8O_6^+$ clusters.

Clusters	Co		
	4*s*	4*p*	3*d*
$Co_6O_4^+$	-0.01	-0.02	2.08
$Co_7O_5^+$	0.00	-0.01	2.36
$Co_8O_6^+$	-0.01	-0.01	2.00

Table S5: Local and total unpaired electrons of the cation $Co_6O_4^+$, $Co_7O_5^+$, and $Co_8O_6^+$ clusters.

Atom	**$Co_6O_4^+$**	**$Co_7O_5^+$**	**$Co_8O_6^+$**
Co (1)	1.96	2.30	2.57
Co (2)	1.87	2.44	1.03
Co (3)	2.15	2.28	2.18
Co (4)	2.20	2.23	2.08
Co (5)	2.06	2.33	2.20
Co (6)	2.00	2.27	1.06
Co (7)	-	2.57	2.20
Co (8)	-	-	2.49
O (1)	0.20	0.28	0.30
O (2)	0.27	0.30	0.21
O (3)	0.09	0.27	0.21
O (4)	0.19	0.38	0.19
O (5)	-	0.36	0.21
O (6)	-	-	0.07
TMM	**13.00**	**18.00**	**17.00**

Table S6. AOs contributions in the SOMOs of the cation $Co_5TMO_4^+$ clusters.

Clusters	TM			Co		
	4s	***4p***	***3d***	***4s***	***4p***	***3d***
$Co_5VO_4^+$	-0.14	-0.03	-2.46	-0.01	-0.02	1.49

$Co_5CrO_4^+$	-0.15	-0.03	-3.68	-0.02	-0.03	2.23
$Co_5MnO_4^+$	-0.11	-0.04	-4.51	-0.01	-0.02	2.22
$Co_5FeO_4^+$	0.02	0.00	3.45	0.00	-0.01	2.28

Table S7. Local and total unpaired electrons of the cation $Co_5TMO_4^+$ clusters.

No.	Atom	$Co_5O_4^+$@ V	$Co_5O_4^+$@ Cr	$Co_5O_4^+$@ Mn	$Co_5O_4^+$@ Fe
1	Co	1.80	2.16	2.16	2.35
2	Co	2.15	2.18	2.19	2.27
3	Co	0.36	2.13	2.25	2.29
4	Co	1.79	2.23	2.17	2.13
5	Co	1.22	2.23	2.20	2.28
6	O	-0.05	0.13	0.31	0.28
7	O	0.13	0.33	0.32	0.28
8	O	0.08	0.32	0.03	0.33
9	O	0.16	0.13	0.04	0.32
10	TM	-2.63	-3.86	-4.66	3.47
Total		**5**	**8**	**7**	**16**

Table S8. AOs contributions in the SOMOs of the cation $Co_6TMO_5^+$ clusters.

Clusters	TM			Co		
	4s	***4p***	***3d***	***4s***	***4p***	***3d***
$Co_6VO_5^+$	0.03	0.00	2.13	0.00	-0.01	1.54
$Co_6CrO_5^+$	0.11	0.03	3.80	0.00	-0.01	2.31
$Co_6MnO_5^+$	-0.10	-0.05	-4.53	0.01	-0.01	2.27
$Co_6FeO_5^+$	0.06	0.00	3.39	0.00	-0.01	2.33

Table S9. Local and total unpaired electrons of the cation $Co_6TMO_5^+$ clusters.

No.	Atom	$Co_6VO_5^+$	$Co_6CrO_5^+$	$Co_6MnO_5^+$	$Co_6FeO_5^+$
1	Co	2.08	2.26	2.25	2.15
2	Co	2.31	2.40	2.35	2.40
3	Co	2.34	2.28	2.26	2.25
4	Co	2.22	2.27	2.23	2.36
5	Co	2.30	2.35	2.22	2.19
6	Co	-2.05	2.27	2.34	2.58
7	O	0.29	0.27	0.04	0.29
8	O	0.27	0.33	0.30	0.36
9	O	0.06	0.27	0.05	0.26
10	O	0.17	0.17	0.39	0.37
11	O	-0.16	0.17	0.27	0.35
12	TM	2.16	3.95	-4.69	3.45
Total		**12**	**19**	**10**	**19**

Table S10. AOs contributions in the SOMOs of the cation $Co_7TMO_6^+$ clusters.

Clusters	TM			Co		
	4s	***4p***	***3d***	***4s***	***4p***	***3d***
$Co_7VO_6^+$	-0.06	-0.02	-1.83	-0.03	-0.02	2.17
$Co_7CrO_6^+$	0.05	0.02	2.78	-0.01	-0.01	2.29
$Co_7MnO_6^+$	0.03	0.00	3.51	0.01	-0.01	2.28
$Co_7FeO_6^+$	0.10	0.00	3.55	-0.01	-0.01	2.37

Table S11. Local and total unpaired electrons of the cation $Co_7TMO_6^+$ clusters.

No.	Atom	$Co_7VO_6^+$	$Co_7CrO_6^+$	$Co_7MnO_6^+$	$Co_7FeO_6^+$
1	Co	2.57	2.62	2.55	2.62
2	Co	2.14	2.11	2.08	2.19
3	Co	2.22	2.13	2.17	2.15
4	Co	2.11	2.11	2.07	2.19
5	Co	2.41	2.38	2.54	2.64
6	Co	2.09	2.12	2.00	2.20
7	Co	2.04	2.39	2.51	2.50
8	O	0.10	0.12	0.19	0.31
9	O	0.32	0.31	0.29	0.33
10	O	0.15	0.12	0.20	0.33
11	O	0.36	0.29	0.33	0.34
12	O	0.19	0.22	0.24	0.22
13	O	0.21	0.24	0.27	0.42
14	TM	-1.91	2.85	3.55	3.57
Total		**15**	**20**	**21**	**22**

Table S12. Cartesian coordinates of optimized $Co_5TMO_4^+$ (TM = V, Cr, Mn and Fe) clusters.

$Co_5TMO_4^+$	X	Y	X
TM = V			
Co	-1.38178900	0.74560700	1.10636800
Co	-1.29513200	-0.73399600	-1.11171300
Co	-0.00202000	1.59035800	-1.17007100
Co	1.36101000	-0.71282400	-1.11277000
Co	1.37629000	0.75283700	1.05496800
V	-0.14517800	-1.65907400	1.21524800
O	1.76248100	1.06967900	-0.77920100
O	-1.74497600	1.04472700	-0.71688900
O	0.03736700	-0.08629000	2.12042500
O	0.03194800	-2.01102600	-0.60636600

TM = Cr

Co	-1.37490300	0.79000500	1.17605300
Co	-1.38878800	-0.74507400	-1.08137400
Co	-0.04049800	1.58785700	-1.07889400
Co	-0.08614200	-1.45497700	1.07686200
Co	1.21295800	0.78790000	1.07787100
Cr	1.64181000	-0.94702200	-1.29539300
O	1.70151800	0.82013300	-0.74382700
O	-1.77436700	1.03324000	-0.64784700
O	-0.02914500	0.00976100	2.26668500
O	0.13755900	-1.88182500	-0.75013400

TM = Mn

Co	-1.34967100	0.69217600	1.15387800
Co	-1.32963600	-0.77822900	-1.12251400
Co	-0.07113500	1.61728800	-1.05321200
Co	1.26075800	-0.60556200	-1.18442000
Co	1.29376300	0.83204100	1.01152800
Mn	0.06371400	-1.79342000	1.21345800
O	1.75615300	1.16900200	-0.78727500
O	-1.79940500	0.97285500	-0.65703100
O	0.08789000	-0.11167200	2.11501700
O	0.08756900	-1.99448300	-0.68942700

TM = Fe

Co	-1.30585600	0.86561700	1.12834600
Co	-1.30925600	-0.83092900	-1.12721600
Co	0.10194700	-1.62796900	1.15176100
Co	1.26508400	0.77877100	1.06285200
Co	1.28961500	-0.75968100	-1.09585300
Fe	-0.03521800	1.65232400	-1.13879800
O	1.70969800	1.08087700	-0.77742100
O	-1.76433100	0.95356100	-0.71337400
O	-0.00479100	-0.03167900	2.16999900
O	0.05310900	-2.08089500	-0.66029600

Table S13. Cartesian coordinates of optimized $Co_6TMO_5^+$ (TM = V, Cr, Mn and Fe) clusters.

$Co_6TMO_5^+$	X	Y	Z

TM = V

Co	-1.33594500	-1.42814200	-0.11979700
Co	0.48725800	-0.33050700	-2.12941800
Co	0.74110600	1.86705800	-0.67649100
Co	-1.23940400	0.69984200	1.38339000
Co	-1.62334700	0.89563500	-1.24443800
Co	2.33875700	-0.45631300	-0.22506900

V	0.64456700	-1.99823200	1.69973800
O	-0.97394700	2.03442600	0.11210500
O	-1.29716200	-0.86483900	-1.90619400
O	-1.01750600	-1.17134900	1.71889400
O	1.91319700	0.74201100	-1.57912600
O	2.23015200	-1.58258400	1.21255500

TM = Cr

Co	0.83499300	1.53489200	-1.31089000
Co	1.22750700	-0.90679200	0.00035500
Co	-0.63060900	-0.45315400	-1.88363400
Co	-0.63051800	-0.45388600	1.88449700
Co	-1.41837000	1.68219600	0.00014500
Co	0.83422700	1.53483800	1.30971100
Cr	-0.32648700	-3.19476700	-0.00014000
O	-1.01740100	1.37688800	1.78860600
O	1.99902300	0.86802400	-0.00003200
O	-1.01705200	1.37712900	-1.78879300
O	0.17933200	-2.03139300	1.36375100
O	0.17893700	-2.03089300	-1.36357600

TM = Mn

Co	0.68702900	1.91190300	-1.31558800
Co	1.92892500	-0.51541400	-0.87902200
Co	-0.43087600	-0.52181600	-1.76572700
Co	-0.99103100	-0.66139800	1.99000500
Co	1.01409100	1.43679500	1.07984600
Co	-0.30338500	-2.35320200	0.27008600
Mn	-1.76488500	1.26884900	0.19217600
O	-0.66978700	1.18449300	1.78909200
O	2.19184000	1.25018500	-0.33046700
O	-1.05411000	1.26749000	-1.59947200
O	-1.18565500	-2.39693400	1.80653100
O	0.70098300	-1.89811400	-1.23745800

TM = Fe

Co	-1.65368800	-1.53364000	0.02020400
Co	0.65122600	-0.76508400	-1.26313900
Co	0.68821000	1.80501800	-0.61499400
Co	-1.31416100	0.71539000	1.25621000
Co	-1.66901000	0.81893100	-1.29103900
Co	3.13657600	-0.26573000	-0.27973400
Fe	0.53478500	-1.56653100	1.37164700
O	-1.04001700	2.07473800	0.03956000
O	-1.24292400	-0.95035900	-1.68140100
O	-1.20449900	-1.08509400	1.84386300
O	2.03691500	0.75974200	-1.32172000
O	1.94431400	-1.60037400	0.16669100

Table S14. Cartesian coordinates of optimized $Co_7TMO_6^+$ (TM = V, Cr, Mn and Fe) clusters.

$Co_7TMO_6^+$	X	Y	Z
TM = V			
Co	0.03755000	-1.75216000	1.30427300
Co	1.17128200	1.24533800	-1.17008200
Co	-1.24049800	-1.28233400	-1.16038700
Co	-1.26766400	1.25903600	-1.29236600
Co	-2.11119000	0.03921900	0.93441200
Co	1.23001200	-1.32271200	-1.23762600
Co	2.39876700	0.01253900	0.75974400
V	0.02669300	1.65612900	1.44525000
O	1.65631000	1.81128300	0.59971200
O	1.79704800	-1.72598100	0.49242300
O	-1.55825700	1.87032100	0.47544600
O	-1.74803700	-1.80280200	0.54325000
O	-0.02413100	-0.05167500	-2.09614900
O	-0.36788600	0.04380100	2.10836000
TM = Cr			
Co	0.00587200	-1.89122700	1.35917900
Co	1.21295800	1.26257100	-1.23601700
Co	-1.24177300	-1.29832500	-1.21856400
Co	-1.21360600	1.26364400	-1.23612600
Co	-2.00585000	0.00080300	0.87239100
Co	1.22131300	-1.29863100	-1.19258500
Co	1.99549700	0.00177800	0.88404100
Cr	0.00226800	1.81863900	1.46962000
O	1.57682000	1.88974100	0.53810300
O	1.72891800	-1.84552800	0.53037600
O	-1.57409800	1.88549600	0.54282700
O	-1.72666100	-1.83680300	0.51402500
O	0.00149700	-0.02608200	-2.09229200
O	0.01684300	0.07392400	1.97128400
TM = Mn			
Co	0.01358000	-1.86948400	1.23795500
Co	1.35362100	1.31772700	-1.15197500
Co	-1.34576500	-1.31898900	-1.22666200
Co	-1.25477700	1.21351300	-1.18644200
Co	-2.05478100	-0.04067100	1.06953600
Co	1.15084100	-1.26065200	-1.15074600
Co	2.12364000	-0.02397800	0.94868200
Mn	-0.00228800	1.81099900	1.06529200
O	1.80227900	1.85127400	0.64262000

O	1.77542400	-1.84770400	0.52926500
O	-1.81007700	1.80405700	0.54999400
O	-1.77862500	-1.84373000	0.55952800
O	0.06567300	0.08917100	-1.96849300
O	-0.03874700	0.11846700	1.78770700

TM = Fe

Co	1.28500700	1.28995500	-1.15664500
Co	-1.27000500	-1.26140500	-1.20073300
Co	-1.25281500	1.25440100	-1.17718900
Co	-1.95637300	0.00056000	1.16537000
Co	1.25621100	-1.25399600	-1.18709800
Co	1.96605500	-0.01448700	1.06147100
Co	-0.00540500	1.96698300	1.08987500
Fe	0.00744400	-1.91796200	1.25412700
O	1.82703800	1.82058300	0.55500500
O	1.78407500	-1.86172300	0.50294300
O	-1.84269200	1.78178500	0.51981000
O	-1.80241300	-1.80456000	0.47215300
O	0.01052500	0.01191500	-2.02847100
O	-0.00665200	-0.01204800	1.83564000