Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

CO Ligands Stabilize Metal Chalcogenide $Co_6Se_8(CO)_n$ Clusters Via Demagnetization

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Cluster	ΔE (eV)	<Co_b-Co_b>	<Co_c-Co_b>	<Se-Co>	Co_c-Co_c
Co_6Se_8		2.60	2.60	2.35	3.57
$Co_6Se_8(CO)$		2.50	2.62	2.35	3.86
trans-$Co_6Se_8(CO)_2$	0.06	2.48	2.65	2.35	3.98
cis-$Co_6Se_8(CO)_2$	Ground State	2.55	2.59	2.35	3.84
fac-$Co_6Se_8(CO)_3$	Ground State	2.65	2.65	2.35	3.75
mer-$Co_6Se_8(CO)_3$	0.11	2.54	2.89	2.35	3.01
trans-$Co_6Se_8(CO)_4$	Ground State	3.08	2.50	2.35	2.45
cis-$Co_6Se_8(CO)_4$	0.29	2.68	2.75	2.35	3.71
$Co_6Se_8(CO)_5$		2.84	2.74	2.35	3.70
$Co_6Se_8(CO)_6$		2.81	2.81	2.35	3.98

Table S1. The average bond length between Co-Co, Co-Se and Co_c-Co_c where Co_b and Co_c are the base and capping atom of $Co_6Se_8(CO)_n$ (n=0-6) clusters.

Clusters	ΔE (eV)	Hirshfeld Charge (Co_6Se_8)	Hirshfeld Charge (CO ligands)
Co_6Se_8		NA	NA
$Co_6Se_8(CO)$		-0.0139	0.0074
trans-$Co_6Se_8(CO)_2$	0.06	-0.0301	0.029
cis-$Co_6Se_8(CO)_2$	Ground State	-0.0128	0.0106
mer-$Co_6Se_8(CO)_3$	0.11	-0.0183	0.018
fac-$Co_6Se_8(CO)_3$	Ground State	-0.024	0.0226
trans-$Co_6Se_8(CO)_4$	Ground State	-0.0133	0.0158
cis-$Co_6Se_8(CO)_4$	0.29	-0.0394	0.0396
$Co_6Se_8(CO)_5$		-0.0472	0.0427
$Co_6Se_8(CO)_6$		-0.0508	0.0461

Table S2. The Hirshfeld charges on Co_6Se_8 and CO ligands in $Co_6Se_8(CO)_n$ (n=0-6) clusters.

Co_6Se_8			$Co_6Se_8(CO)$		
Spin-state	Energy (eV)	ΔE (eV)	Spin-state	Energy (eV)	ΔE (eV)
4	-84.19969769	0.839	6	-101.75573212	0.095
8	-84.57226774	0.466	8 (GS)	-101.85098311	0.000
10 (GS)	-85.03890472	0.00	10	-101.48737762	0.363
12	-84.72927066	0.309			
cis-$Co_6Se_8(CO)_2$			*fac*-$Co_6Se_8(CO)_3$		
6	-118.65222575	0.081	4	-135.65278584	0.382
8(GS)	-118.7335321	0.000	6 (GS)	-136.03496991	0.000
10	-118.33357007	0.399	8	-135.52419811	0.510
trans-$Co_6Se_8(CO)_4$			$Co_6Se_8(CO)_5$		
2	-153.44822303	0.103	0	-169.60567551	0.881
4 (GS)	-153.55185644	0.000	2 (GS)	-170.48728969	0.000
6	-152.91415708	0.637	4	-169.73651692	0.750
$Co_6Se_8(CO)_6$					
0 (GS)	-188.12391783	0.000			
2	-187.06687971	1.057			

Table S3. The absolute total energy of $Co_6Se_8(CO)_n$ (n=0-6) in different spin states are given. The ground state of clusters is indicated by "GS" and relative energies with respect to ground states are also added.

Cluster	**Moment (μ_B)**	**Energy (eV)**
Co_6Se_8; nosym	10	-85.03890472
Co_6Se_8; C_{4v}	10	-85.02805818
Co_6Se_8; C_{2v}	10	-85.04174434
$Co_6Se_8(CO)$;nosym	8	-101.85098311
$Co_6Se_8(CO)$;C_{4v}	8	-101.85064612
***cis*-$Co_6Se_8(CO)_2$;nosym**	8	**-118.73353210**
***cis*-$Co_6Se_8(CO)_2$; C(s)**	8	-118.73326928
***cis*-$Co_6Se_8(CO)_2$; C_{2v}**	8	-118.53981304
***fac*-$Co_6Se_8(CO)_3$;nosym**	6	-136.03496991
***fac*-$Co_6Se_8(CO)_3$;C_{3v}**	6	-136.01691305
***trans*-$Co_6Se_8(CO)_4$;nosym**	4	-153.55185644
***trans*-$Co_6Se_8(CO)_4$; D_{2h}**	4	-153.55169637
***trans*-$Co_6Se_8(CO)_4$; D_{4h}**	4	-153.55146749

$Co_6Se_8(CO)_5$;nosym	2	-170.48728969
$Co_6Se_8(CO)_5;C_{4v}$	2	-170.17183552
$Co_6Se_8(CO)_5;C_s$	2	-170.45145592
$Co_6Se_8(CO)_6$;nosym	0	-188.12391783
$Co_6Se_8(CO)_6;O_h$	0	-188.12353938
$Co_6Se_8(CO)_6;C_{4v}$	0	-188.12285364

Table S4. The absolute total energy of $Co_6Se_8(CO)_n$ (n=0-6) with different point group symmetries.

Summary of Natural Population Analysis:

Atom No	Natural Charge	Natural Population			
		Core	Valence	Rydberg	Total
Co 1	0.02655	17.99109	8.90753	0.07483	26.97345
Co 2	0.02658	17.99109	8.90750	0.07483	26.97342
Co 3	0.02618	17.99109	8.90780	0.07493	26.97382
Co 4	0.02612	17.99109	8.90785	0.07494	26.97388
Co 5	0.02610	17.99109	8.90787	0.07494	26.97390
Co 6	0.02603	17.99109	8.90793	0.07495	26.97397
Se 7	-0.09194	27.99828	6.04537	0.04829	34.09194
Se 8	-0.09187	27.99828	6.04530	0.04830	34.09187
Se 9	-0.09195	27.99828	6.04538	0.04829	34.09195
Se 10	-0.09187	27.99828	6.04530	0.04830	34.09187
Se 11	-0.09188	27.99828	6.04530	0.04830	34.09188
Se 12	-0.09183	27.99828	6.04525	0.04830	34.09183
Se 13	-0.09190	27.99828	6.04533	0.04830	34.09190
Se 14	-0.09182	27.99828	6.04524	0.04830	34.09182
C 15	0.53182	1.99937	3.41674	0.05206	5.46818
C 16	0.53143	1.99937	3.41690	0.05230	5.46857
C 17	0.53143	1.99937	3.41688	0.05231	5.46857
C 18	0.53188	1.99937	3.41668	0.05207	5.46812
C 19	0.53142	1.99937	3.41690	0.05231	5.46858
C 20	0.53145	1.99937	3.41687	0.05231	5.46855
O 21	-0.43572	1.99977	6.39676	0.03919	8.43572
O 22	-0.43515	1.99977	6.39717	0.03821	8.43515
O 23	-0.43513	1.99977	6.39715	0.03821	8.43513
O 24	-0.43514	1.99977	6.39716	0.03821	8.43514
O 25	-0.43567	1.99977	6.39670	0.03920	8.43567
O 26	-0.43513	1.99977	6.39714	0.03821	8.43513
* Total *	-0.00000	355.92763	160.69197	1.38040	518.00000

Atom No	Natural Electron Configuration
Co 1	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Co 2	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Co 3	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Co 4	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Co 5	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Co 6	[core]4s(0.56)3d(8.35)4p(0.04)5s(0.01)4d(0.02)5p(0.01)
Se 7	[core]4s(1.86)4p(4.19)4d(0.03)
Se 8	[core]4s(1.86)4p(4.19)4d(0.03)
Se 9	[core]4s(1.86)4p(4.19)4d(0.03)
Se 10	[core]4s(1.86)4p(4.19)4d(0.03)
Se 11	[core]4s(1.86)4p(4.19)4d(0.03)
Se 12	[core]4s(1.86)4p(4.19)4d(0.03)
Se 13	[core]4s(1.86)4p(4.19)4d(0.03)
Se 14	[core]4s(1.86)4p(4.19)4d(0.03)

C 15	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
C 16	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
C 17	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
C 18	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
C 19	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
C 20	[core]2s(1.22)2p(2.19)3s(0.02)3p(0.03)
O 21	[core]2s(1.71)2p(4.69)3d(0.03)
O 22	[core]2s(1.71)2p(4.69)3d(0.03)
O 23	[core]2s(1.71)2p(4.69)3d(0.03)
O 24	[core]2s(1.71)2p(4.69)3d(0.03)
O 25	[core]2s(1.71)2p(4.69)3d(0.03)
O 26	[core]2s(1.71)2p(4.69)3d(0.03)

Table S5. Summary of Natural Population Analysis (NBO) of $Co_6Se_8(CO)_6$.

$Co_6Se_8(CO)_6$ (O_h)

$A_{1g}^{12}\ A_{2g}^{2}E_g^{20}T_{1g}^{18}T_{2g}^{30}A_{2u}^{4}A_{1u}^{0}E_u^{4}T_{1u}^{24}T_{2u}^{48}$

$Co_6Se_8(CO)_6$ (C_{4v})

$A_1^{38}\ A_2^{8}\ B_1^{20}\ B_2^{16}\ E_1^{80}$

Total =162 e^-

$Co_6Se_8(CO)_5$ (C_{4v})

Alpha

$A_1^{17}\ A_2^{4}\ B_1^{10}\ B_2^{8}\ E_1^{38}$

Beta

$A_1^{17}\ A_2^{4}\ B_1^{10}\ B_2^{8}\ E_1^{36}$

Total =152 e^-

***trans*-$Co_6Se_8(CO)_4$ (D_{2h})**

Alpha

$A_g^{15}\ A_u^{4}\ B_{1g}^{8}\ B_{2g}^{7}\ B_{3g}^{7}\ B_{1u}^{10}\ B_{2u}^{11}\ B_{3u}^{11}$

Beta

$A_g^{15}\ A_u^{4}\ B_{1g}^{8}\ B_{2g}^{6}\ B_{3g}^{6}\ B_{1u}^{8}\ B_{2u}^{11}\ B_{3u}^{11}$

Total =142 e^-

***fac*-$Co_6Se_8(CO)_3$ (C_{3v})**

Alpha

$A_1^{18}\ A_2^{7}\ E^{44}$

Beta

$A_1^{17}A_2^{6}E^{40}$

Total =132 e^-

***cis*-$Co_6Se_8(CO)_2$ (C_{2v})**

Alpha

$A_1^{22}\ A_2^{11}\ B_1^{15}\ B_2^{17}$

Beta

$A_1^{19}\ A_2^{9}\ B_1^{14}\ B_2^{15}$

Total =122 e^-

$Co_6Se_8(CO)$ (C_{4v})
Alpha
$A_1^{13}\ A_2^{3}\ B_1^{7}\ B_2^{7}\ E_1^{30}$
Beta
$A_1^{12}\ A_2^{2}\ B_1^{5}\ B_2^{7}\ E_1^{26}$
Total =112 e-
Co_6Se_8 (C_{4v})
Alpha
$A_1^{11}\ A_2^{3}\ B_1^{7}\ B_2^{7}\ E_1^{28}$
Beta
$A_1^{10}\ A_2^{2}\ B_1^{5}\ B_2^{7}\ E_1^{22}$
Total =102 e^-

Table S6. Electronic Configuration of $Co_6Se_8(CO)_n$ Clusters.

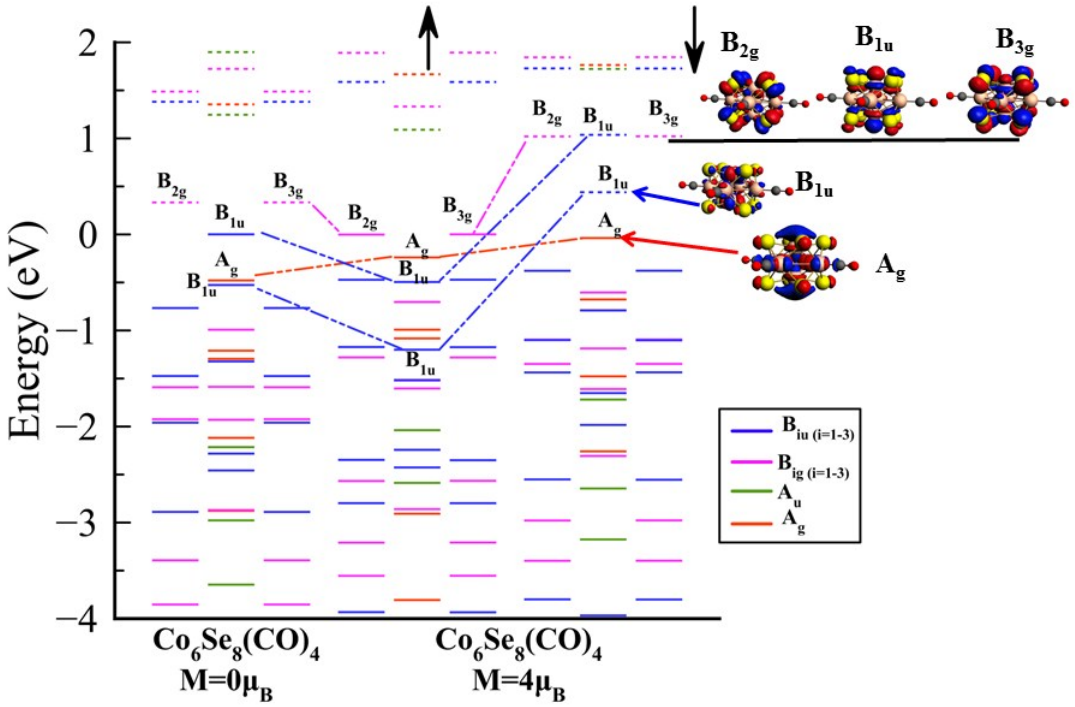

Fig. S1. One electron energy levels of *trans*-$Co_6Se_8(CO)_4$. The solid and dashed lines represent the occupied and unoccupied energy levels. Up and down arrows indicate the majority and minority spin channel.

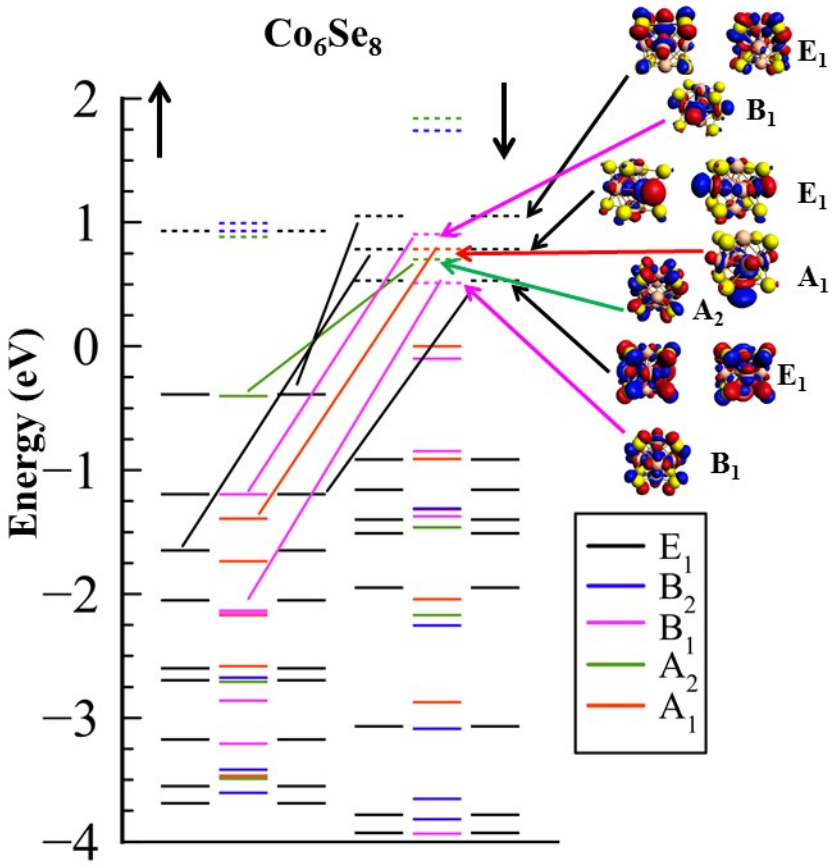

Fig. S2. One electron energy levels of Co_6Se_8. The solid and dashed lines represent the occupied and unoccupied energy levels. Up and down arrows indicate the majority and minority spin channel.

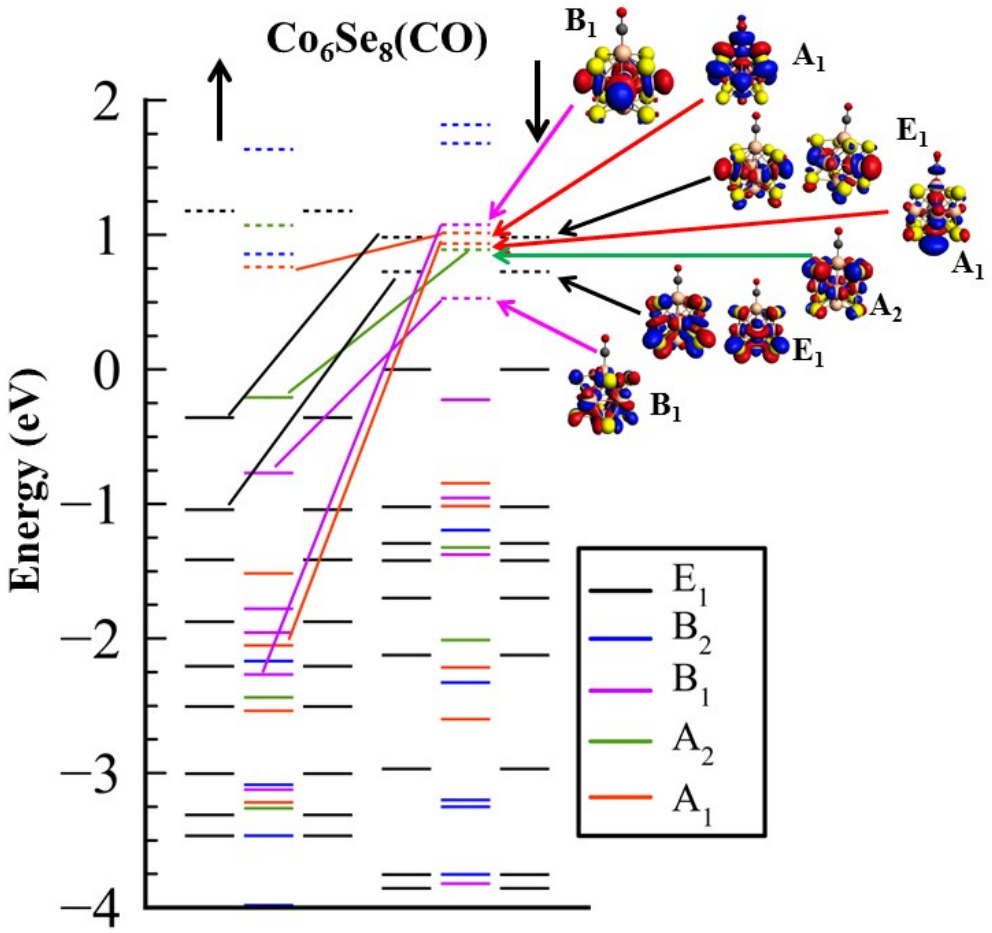

Fig. S3. One electron energy levels of $Co_6Se_8(CO)$. The solid and dashed lines represent the occupied and unoccupied energy levels. Up and down arrows indicate the majority and minority spin channel.

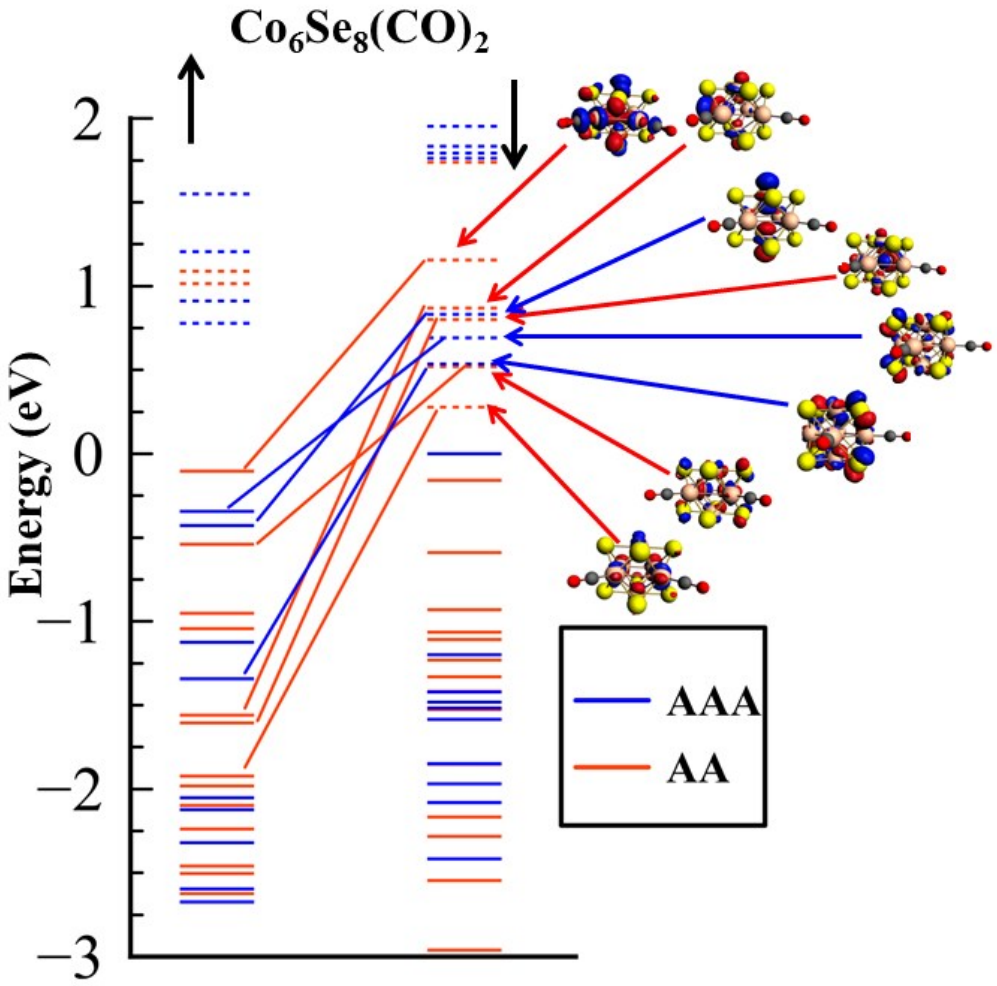

Fig. S4. One electron energy levels of *cis*-$Co_6Se_8(CO)_2$. The solid and dashed lines represent the occupied and unoccupied energy levels. Up and down arrows indicate the majority and minority spin channel.

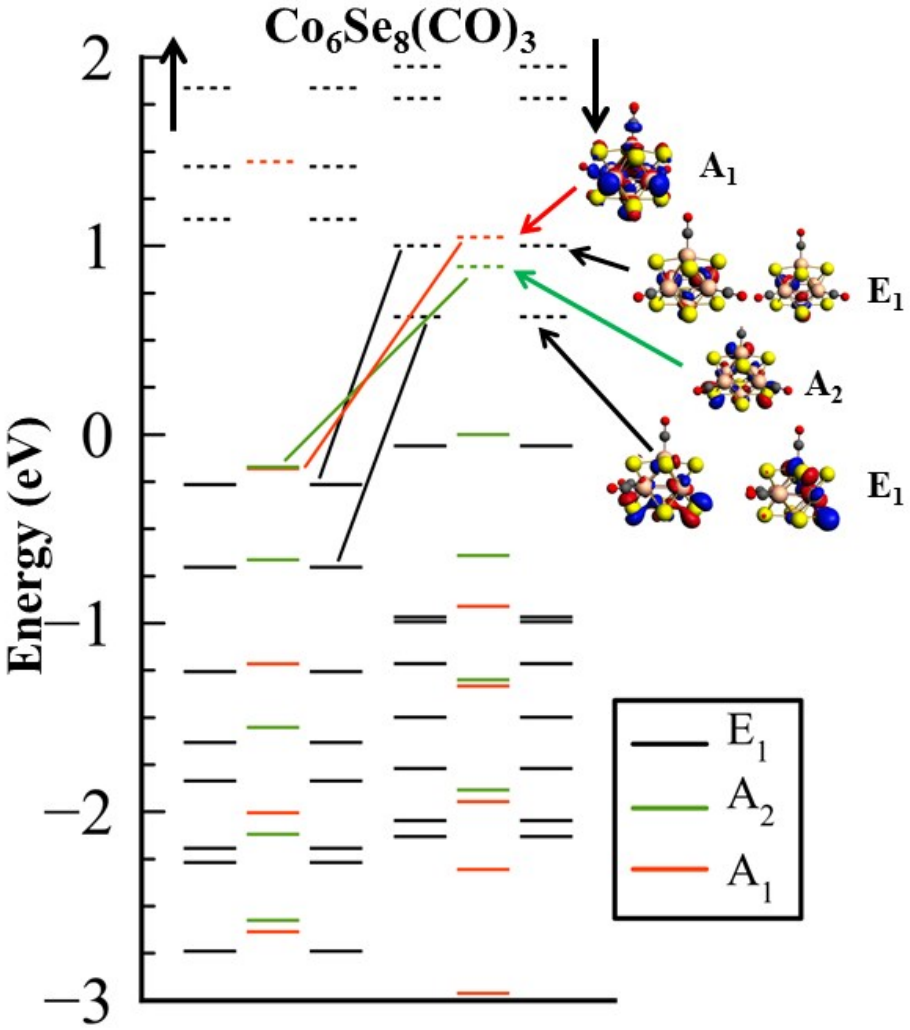

Fig. S5. One electron energy levels of *fac*-$Co_6Se_8(CO)_3$. The solid and dashed lines represent the occupied and unoccupied energy levels. Up and down arrows indicate the majority and minority spin channel.

Optimized Cartesian co-ordinates of $Co_6Se_8(CO)_n$ (n=0-6) clusters

Co_6Se_8

14
ADF XYZ
Co -3.7E-05 0.000992 0.032644
Co -0.001269 0.003578 3.61204
Co 1.767867 -0.007932 1.846738
Co 0.002234 -1.77515 1.84262
Co -1.766821 0.000519 1.846311
Co -0.005483 1.775462 1.846628
Se 1.66095 -1.663033 3.50993
Se -1.653851 1.647565 0.166062
Se 1.669369 1.664085 3.4922
Se -1.661684 -1.667195 3.497135
Se -1.665683 1.665346 3.501918
Se 1.654213 1.652441 0.180125
Se 1.650467 -1.65255 0.161315
Se -1.653793 -1.649281 0.167517

$Co_6Se_8(CO)$

16
ADF XYZ
Co 0.000961 0.000122 0.043203
Co -0.00036 0.00089 3.911279
Co 1.771089 -0.000142 1.777462
Co -0.00033 -1.770361 1.7773
Co -1.770366 0.001207 1.776249
Co 0.001072 1.77149 1.776383
Se -1.643354 1.645371 3.448996
Se 1.64304 -1.643607 3.450876
Se 1.673178 -1.673414 0.126611
Se -1.67136 1.673683 0.124691
Se 1.674496 1.672419 0.125753
Se -1.672583 -1.672162 0.125479
Se -1.644721 -1.642396 3.449776
Se 1.644201 1.644091 3.450142
C -0.000993 0.001384 5.620061
O -0.001432 0.001674 6.764934

***trans*-$Co_6Se_8(CO)_2$**

18
ADF XYZ
Co -0.001027 -9.7E-05 0.057379
Co -0.000165 0.000103 4.041953
Co 1.759853 -0.000295 2.049233
Co -0.001301 -1.759779 2.049246
Co -1.760631 0.000344 2.049852
Co -0.000643 1.759452 2.050071
Se 1.668438 1.66827 3.674659
Se -1.668533 1.667361 3.676458
Se 1.667744 -1.66957 3.674285
Se -1.668687 -1.668001 3.675678
Se -1.669895 -1.667213 0.423288
Se 1.667005 -1.668189 0.423519
Se 1.66713 1.668718 0.424153
Se -1.669214 1.669065 0.424312
C 0.010709 0.001716 5.767704
O 0.018516 0.002437 6.911012
C 0.006231 -0.001629 -1.669105
O 0.011472 -0.00396 -2.812351

***cis*-$Co_6Se_8(CO)_2$**

` 18
ADF XYZ
Co 0.000123 0.031381 0.073962
Co 0.001331 0.008694 3.922201
Co 1.688848 -0.026144 1.828138
Co -0.066643 -1.749128 1.812878
Co -1.685719 0.101121 1.828712
Co 0.079229 2.066472 1.788528
Se 1.5896 -1.698831 3.478867
Se -1.61071 1.739804 0.149655
Se 1.607537 -1.700733 0.160938
Se 1.737839 1.611532 0.145022
Se -1.736146 -1.577206 0.165751
Se -1.710941 -1.573432 3.481614
Se 1.685645 1.613291 3.489368
Se -1.558066 1.734022 3.491044
C 0.149049 3.837719 1.79235
O 0.193857 4.97922 1.780632
C 0.003576 0.010007 5.660465
O 0.0051 0.004374 6.804427

mer-$Co_6Se_8(CO)_3$

20
ADF XYZ
Co -0.119453 2.8E-05 -0.058137
Co 0.018103 -8.4E-05 3.972119
Co 2.10503 -6.8E-05 1.82097
Co 0.018635 1.5089 1.818153
Co -2.049251 -0.000385 1.729879
Co 0.018868 -1.508448 1.818248
Se -1.633052 1.604637 3.452601
Se 1.657835 1.626663 3.478116
Se 1.658185 -1.626843 3.478552
Se -1.633148 -1.605331 3.453039
Se -1.648809 -1.739855 0.149914
Se 1.617986 -1.599668 0.123524
Se 1.617985 1.599356 0.123428
Se -1.649509 1.739317 0.150308
C 0.008262 0.000375 5.704242
O 0.003914 0.000809 6.849006
C -3.805871 -0.001504 1.696476
O -4.948063 -0.002436 1.663535
C 3.843572 -0.000631 1.810005
O 4.987557 -0.00117 1.802417

***fac*-$Co_6Se_8(CO)_3$**

20
ADF XYZ
Co -0.003976 0.003476 0.055439
Co -0.008734 0.007012 3.808612
Co 1.713667 0.004486 1.771868
Co -0.001231 -1.714607 1.77132
Co -2.039648 0.005782 1.779137
Co -0.011976 2.038426 1.779864
Se -1.646352 -1.659457 3.417464
Se 1.653772 1.648898 3.418569
Se -1.651622 1.646956 0.115469
Se 1.654645 -1.652074 3.442051
Se -1.673149 -1.654054 0.11655
Se -1.653949 1.648235 3.423139
Se 1.66515 -1.661429 0.103729
Se 1.649323 1.676767 0.117577
C -0.023684 0.021434 5.544281
O -0.025447 0.022789 6.688225
C -3.775305 0.019583 1.795094
O -4.919112 0.020525 1.79753
C -0.029065 3.774074 1.796161
O -0.031903 4.918097 1.798536

***trans*-$Co_6Se_8(CO)_4$**

22
ADF XYZ
Co 0.00191 -0.002471 0.022984
Co 0.001485 -0.000727 2.473055
Co 2.183789 -0.007402 1.247749
Co -0.006175 -2.180144 1.247757
Co -2.17904 0.004528 1.247118
Co 0.004298 2.179756 1.24747
Se 1.623224 -1.629962 2.867478
Se -1.627696 -1.620785 2.871091
Se -1.627592 -1.621986 -0.375759
Se 1.628753 1.618979 -0.374466
Se 1.629189 1.620286 2.869151
Se -1.620203 1.625463 -0.3757
Se 1.623856 -1.630878 -0.371552
Se -1.621961 1.627018 2.869667
C -3.92987 0.007732 1.247046
O -5.073276 0.011087 1.247216
C 3.934485 -0.008546 1.248052
O 5.078 -0.011244 1.248306
C 0.005414 3.930348 1.24578
O 0.003289 5.073691 1.243992
C -0.012754 -3.931082 1.248191
O -0.015932 -5.07444 1.248769

***cis*-$Co_6Se_8(CO)_4$**

22
ADF XYZ
Se 9.743474 13.204907 12.441107
Se 15.255125 11.790283 12.59785
Se 11.37012 11.661135 10.045773
Se 13.626596 13.319487 15.05624
Se 12.19563 15.312612 12.802721
Se 12.804662 9.67859 12.239106
Se 11.116555 11.17378 14.693769
Se 13.881805 13.820526 10.414153
Co 11.652894 13.718391 11.139949
Co 13.206386 11.477158 13.663603
Co 10.971952 11.181983 12.327642
Co 14.025655 13.807833 12.768116
Co 11.662357 13.260818 13.766291
Co 13.503255 11.582305 11.019791
C 9.674666 10.053883 12.111737
O 8.819812 9.308075 11.97168

O 10.491556 15.414036 9.137217
C 10.956507 14.738773 9.934989
C 15.324606 14.9408 12.94308
O 16.180397 15.688595 13.066982
C 14.35581 10.843287 9.713453
O 14.930272 10.355317 8.852839

$Co_6Se_8(CO)_5$

24
ADF XYZ
Co 0.001166 -0.076004 -0.010164
Co 0.00042 -0.021012 3.695275
Co 2.029895 0.009261 1.749377
Co 0.000722 -1.976838 1.732245
Co -2.02809 0.009433 1.748613
Co 0.00089 2.018378 1.749543
Se -1.640384 1.646068 3.382032
Se 1.655574 -1.648521 3.364442
Se -1.654669 -1.648421 3.363771
Se 1.641468 1.64592 3.382636
Se -1.614531 1.635683 0.069254
Se 1.706125 -1.65366 0.089712
Se 1.616998 1.635544 0.069922
Se -1.703906 -1.6536 0.089062
C 0.000987 -3.703725 1.655974
O 0.00122 -4.845696 1.604343
C -3.747759 0.067223 1.758537
O -4.891219 0.104974 1.761422
C -8.E-06 -0.012629 5.419689
O -0.000327 -0.009507 6.563423
C 0.000826 3.739519 1.723753
O 0.000684 4.883626 1.703462
C 3.749545 0.067242 1.760305
O 4.892948 0.105179 1.7639

$Co_6Se_8(CO)_6$

26
ADF XYZ
Co 0.002729 -0.000323 0.103968
Co 0.001948 0.001288 4.090653
Co 1.994742 -0.000338 2.097754
Co 0.001062 -1.991764 2.097925
Co -1.990172 0.001325 2.096926
Co 0.002948 1.992489 2.096613
Se 1.645734 1.643645 3.740366
Se -1.642049 -1.641266 3.740879
Se -1.641368 -1.642555 0.454126
Se 1.646447 1.642281 0.453849
Se -1.640529 1.644853 3.739808
Se 1.644273 -1.642694 3.741379
Se 1.64491 -1.643997 0.454991
Se -1.639917 1.643473 0.453042
C 0.001454 0.001036 5.807104
O 0.00112 0.000754 6.951329
C 3.711202 -0.001108 2.097952
O 4.855368 -0.001541 2.098046
C 0.002966 3.708967 2.094979
O 0.002805 4.8531 2.093785
C 0.003295 -0.000164 -1.612471
C 0.001118 -3.708232 2.099416
O 0.00132 -4.852399 2.100483
O 0.003685 6.9E-05 -2.756563
C -3.70664 0.002249 2.096528
O -4.85075 0.00281 2.096271