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

Supporting Information

Investigating cooperative effects in small cobalt and cobalt-nickel alloy clusters with attached ethanol

Fabian Dietrich,[*a,b] Markus Becherer,[b] Daniel Bellaire,[b], Paulina Martínez-Rodríguez,[c], and Markus Gerhards[b]

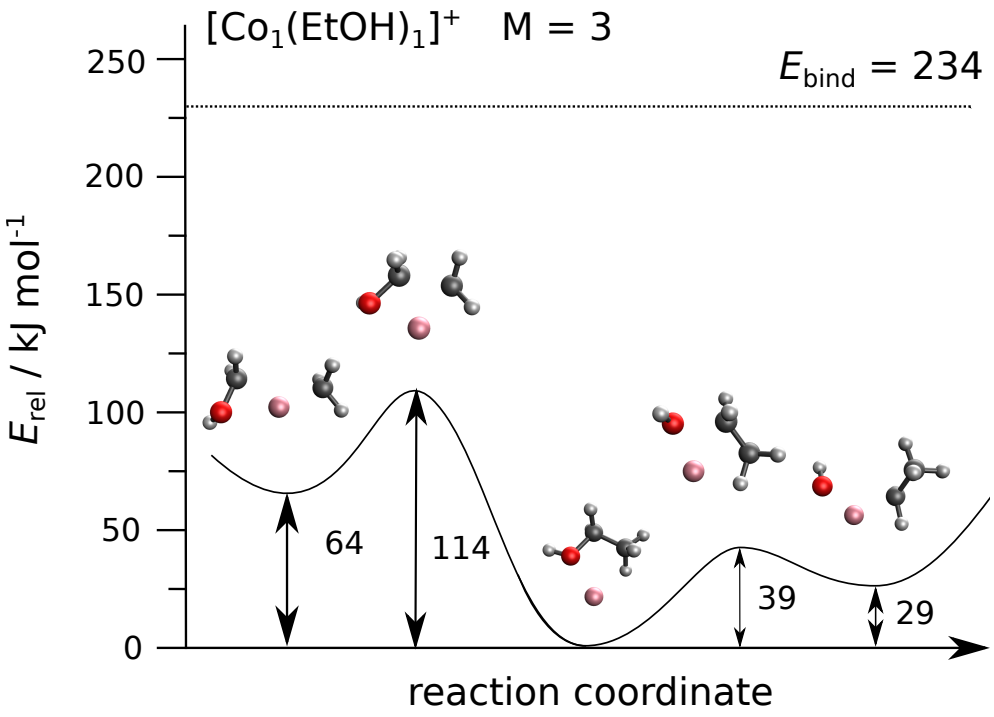

Figure S 1 Calculated reaction pathways for the $[Co_1(EtOH)]^+$ cluster, all energies in kJ/mol.

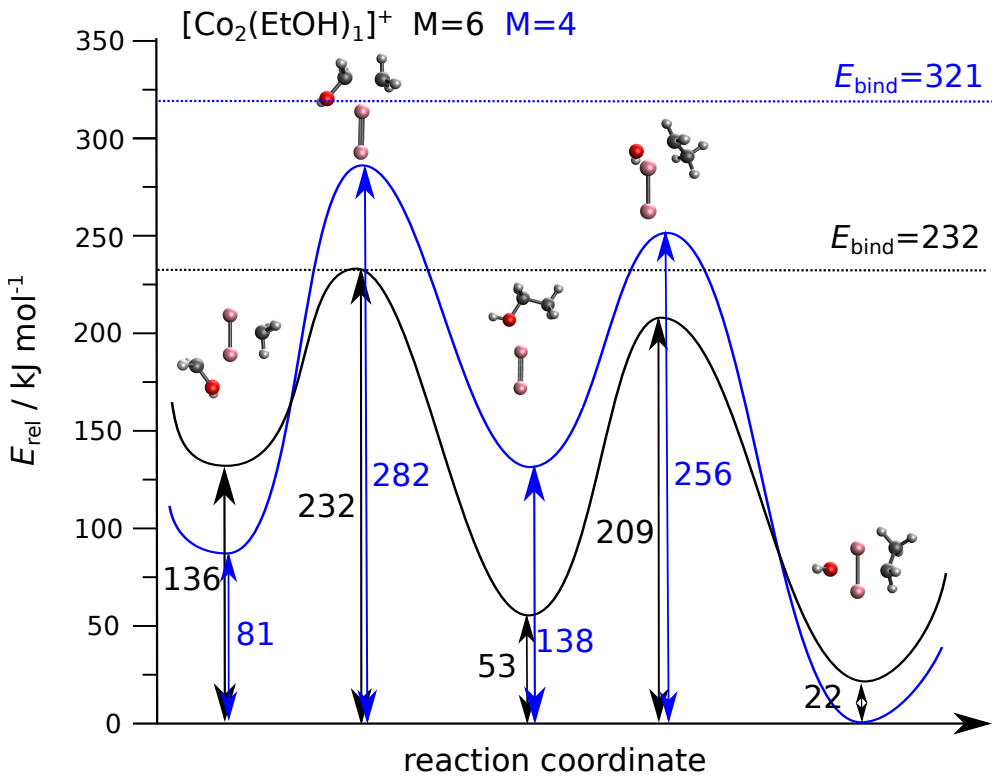

Figure S 2 Calculated reaction pathways for the $[Co_2(EtOH)]^+$ cluster, all energies in kJ/mol.

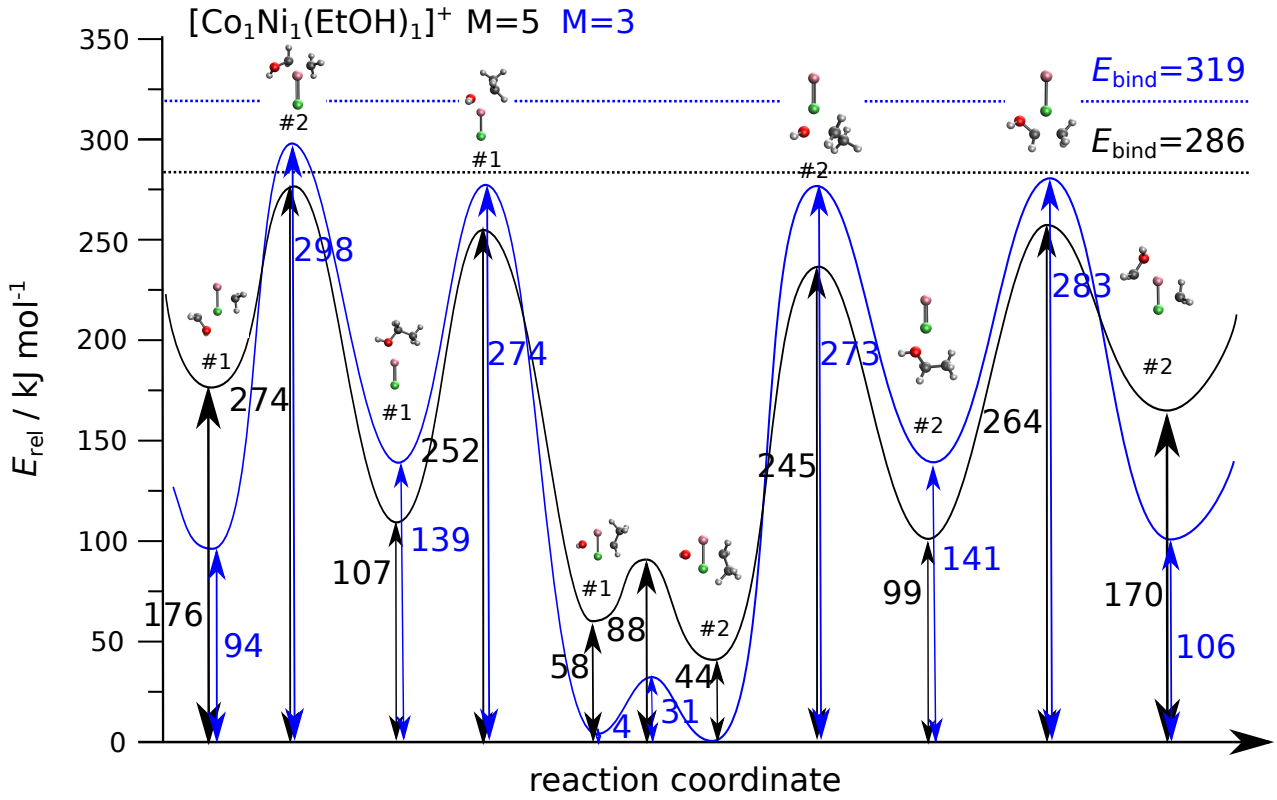

Figure S 3 Calculated reaction pathways for the $[Co_1Ni_1(EtOH)]^+$ cluster, all energies in kJ/mol.

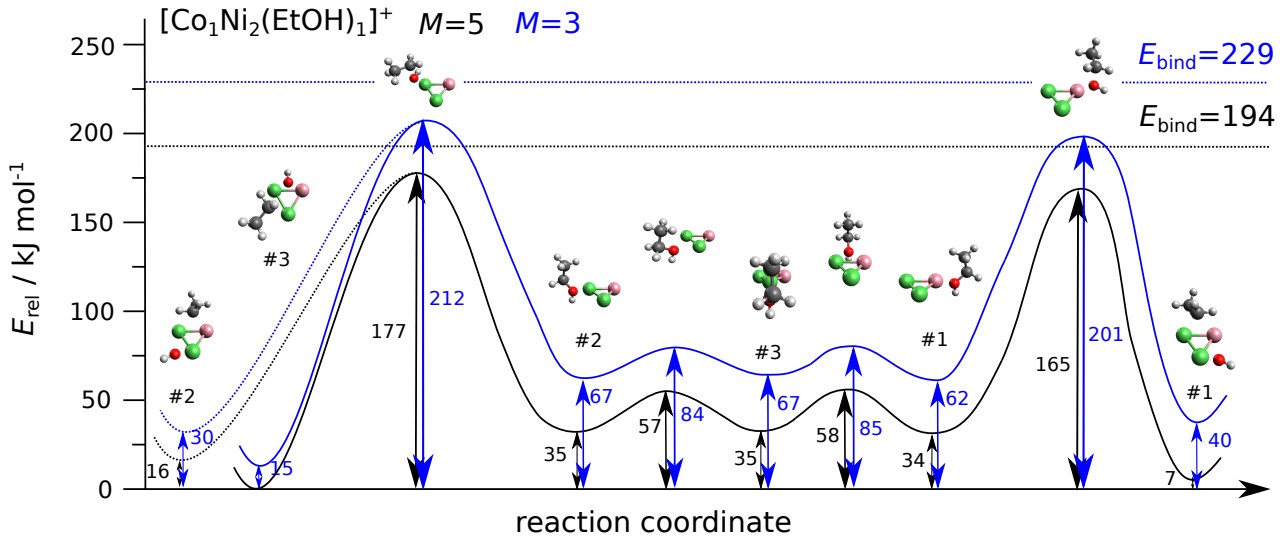

Figure S 4 Calculated reaction pathways for the $[Co_1Ni_2(EtOH)]^+$ cluster, all energies in kJ/mol.

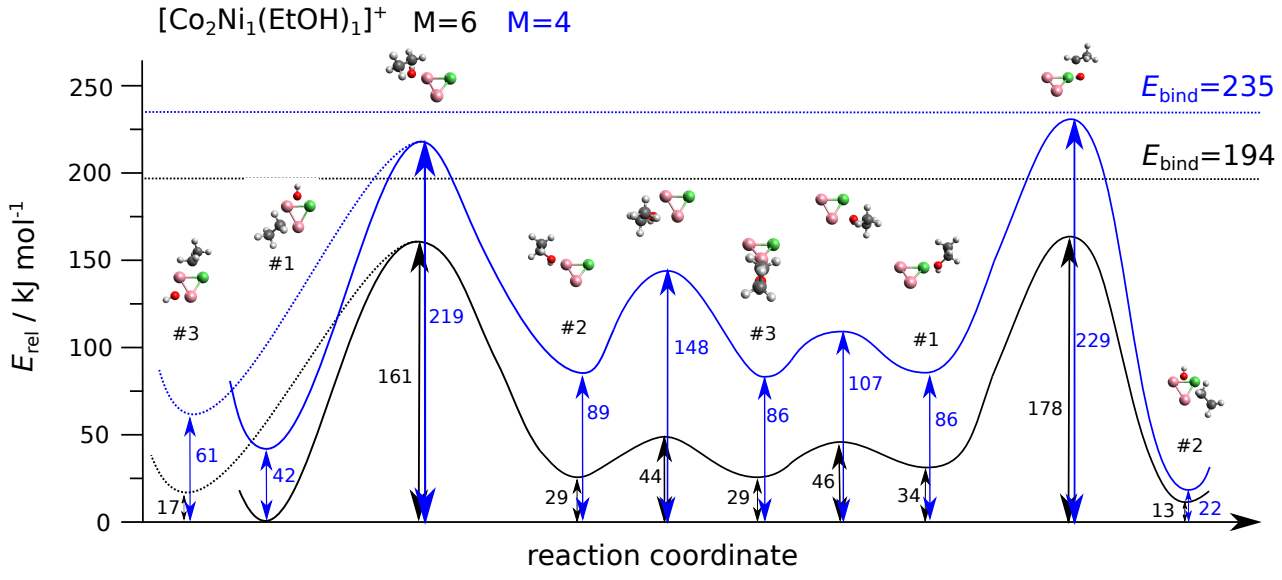

Figure S 5 Calculated reaction pathways for the $[Co_2Ni_1(EtOH)]^+$ cluster, all energies in kJ/mol.

Table S 1 Charge distribution from NBO calculations on optimized structures of $[Co_1(EtOH)_1]^+$ and $[Co_2(EtOH)_1]^+$. The values for $[Co_3(EtOH)_1]^+$ are given for comparison, because they were not given in [15].

cluster core	Co^+	Co^+	$Co_2{}^+$	$Co_2{}^+$	$Co_2{}^+$	$Co_2{}^+$	$Co_3{}^+$
motif	C_2H_5OH	C_2H_5 & OH	C_2H_5OH	C_2H_5 & OH	C_2H_5OH	C_2H_5 & OH	C_2H_5OH
M	3	3	4	4	6	6	7
M1	0.875	1.140	0.573	0.885	0.571	1.006	0.363 (O)
M2	-	-	0.304	0.768	0.310	0.985	0.265
M3	-	-	-	-	-	-	0.264
$\sum$(core)	0.875	1.140	0.877	1.653	0.881	1.991	0.892
O	-0.806	-0.792	-0.820	-1.022	-0.828	-1.136	-0.817
H(O)	0.525	0.489	0.523	0.496	0.523	0.519	0.518
$\sum$(OH)	-0.281	-0.303	-0.297	-0.526	-0.305	-0.617	-0.299
C_1	-0.069	-0.408	-0.054	-0.677	-0.053	-0.900	-0.054
$H_1(C_1)$	0.222	0.196	0.208	0.246	0.208	0.262	0.204
$H_2(C_1)$	0.210	0.239	0.209	0.208	0.208	0.211	0.202
C_2	-0.653	-0.669	-0.659	-0.622	-0.656	-0.645	-0.651
$H_1(C_2)$	0.247	0.252	0.225	0.266	0.225	0.245	0.260
$H_2(C_2)$	0.289	0.263	0.267	0.178	0.265	0.223	0.224
$H_3(C_2)$	0.161	0.289	0.223	0.275	0.225	0.229	0.221
$\sum$(EtOH)	0.126	-0.141	0.122	-0.652	0.117	-0.992	0.107

Table S 2 Charge distribution from NBO calculations on optimized structures of $[Co_1Ni_1(EtOH)_1]^+$.

cluster core	$CoNi^+$	$CoNi^+$	$CoNi^+$	$CoNi^+$
motif	C_2H_5OH #1	C_2H_5OH #2	C_2H_5 & OH #1	C_2H_5 & OH #1
M	5	5	3	5
M1	0.604 (Co)	0.484 (Ni)	0.866 (Co)	1.050 (Co)
M2	0.265 (Ni)	0.383 (Co)	0.747 (Ni)	0.926 (Ni)
M3	-	-	-	-
$\sum$(core)	0.869	0.867	1.613	1.976
O	-0.820	-0.812	-1.001	-1.132
H(O)	0.524	0.523	0.496	0.521
$\sum$(OH)	-0.296	-0.289	-0.505	-0.611
C_1	-0.055	-0.054	-0.663	-0.857
$H_1(C_1)$	0.208	0.207	0.215	0.176
$H_2(C_1)$	0.212	0.209	0.248	0.254
C_2	-0.659	-0.656	-0.632	-0.645
$H_1(C_2)$	0.269	0.223	0.177	0.229
$H_2(C_2)$	0.228	0.228	0.267	0.247
$H_3(C_2)$	0.223	0.264	0.279	0.232
$\sum$(EtOH)	0.130	0.132	-0.614	-0.975

Table S 3 Charge distribution from NBO calculations on optimized structures of $[Co_1Ni_2(EtOH)_1]^+$.

cluster core	$CoNi_2{}^+$	$CoNi_2{}^+$	$CoNi_2{}^+$	$CoNi_2{}^+$	$CoNi_2{}^+$
motif	C_2H_5OH #1	C_2H_5OH #2	C_2H_5 & OH #1	C_2H_5 & OH #3	C_2H_5 & OH #2
M	5	5	5	5	5
M1	0.450 (Co-O)	0.320 (Ni-O)	0.652 (Ni-O)	0.810 (Co-O)	0.636 (Ni-O)
M2	0.213 (Ni)	0.355 (Co)	0.795 (Co-O,C)	0.632 (Ni-O,C)	0.649 (Ni-O,C)
M3	0.213 (Ni)	0.218 (Ni)	0.391 (Ni-C)	0.340 (Ni-C)	0.558 (Co-C)
$\sum$(core)	0.876	0.893	1.838	1.782	1.843
O	-0.813	-0.814	-1.091	-1.112	-1.082
H(O)	0.518	0.517	0.495	0.503	0.493
$\sum$(OH)	-0.295	-0.297	-0.596	-0.609	-0.589
C_1	-0.055	-0.055	-0.723	-0.568	-0.756
$H_1(C_1)$	0.205	0.205	0.244	0.234	0.247
$H_2(C_1)$	0.205	0.201	0.183	0.103	0.200
C_2	-0.655	-0.651	-0.673	-0.674	-0.660
$H_1(C_2)$	0.264	0.26	0.261	0.262	0.253
$H_2(C_2)$	0.223	0.226	0.233	0.237	0.231
$H_3(C_2)$	0.223	0.219	0.232	0.232	0.230
$\sum$(EtOH)	0.115	0.108	-0.839	-0.783	-0.844

Table S 4 Charge distribution from NBO calculations on optimized structures of $[Co_2Ni_1(EtOH)_1]^+$.

cluster core	Co_2Ni^+	Co_2Ni^+	Co_2Ni^+	Co_2Ni^+	Co_2Ni^+
motif	C_2H_5OH #2	C_2H_5OH #1	C_2H_5 & OH #2	C_2H_5 & OH #1	C_2H_5 & OH #3
M	6	6	6	6	6
M1	0.408 (Co-O)	0.279 (Ni-O)	0.758 (Co-O)	0.767 (Co-O)	0.582 (Ni-O)
M2	0.298 (Co)	0.308 (Co)	0.610 (Ni-O,C)	0.749 (Co-O,C)	0.746 (Co-O,C)
M3	0.185 (Ni)	0.309 (Co)	0.483 (Co-C)	0.322 (Ni-C)	0.515 (Co-C)
$\sum$(core)	0.891	0.896	1.851	1.848	1.843
O	-0.818	-0.818	-1.108	-1.113	-1.075
H(O)	0.518	0.516	0.499	0.501	0.494
$\sum$(OH)	-0.300	-0.302	-0.609	-0.612	-0.581
C_1	-0.054	-0.054	-0.736	-0.708	-0.750
$H_1(C_1)$	0.203	0.203	0.244	0.245	0.249
$H_2(C_1)$	0.205	0.202	0.199	0.186	0.197
C_2	-0.652	-0.649	-0.664	-0.672	-0.657
$H_1(C_2)$	0.261	0.258	0.255	0.260	0.252
$H_2(C_2)$	0.225	0.223	0.230	0.232	0.229
$H_3(C_2)$	0.221	0.222	0.230	0.231	0.227
$\sum$(EtOH)	0.109	0.103	-0.851	-0.838	-0.834

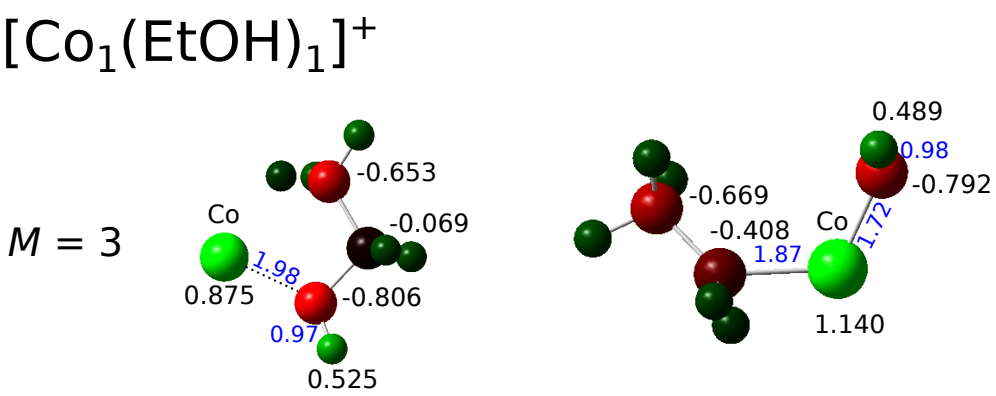

Figure S 6 Charge distribution from NBO calculations (positive: green; negative: red) and atomic distances (blue; in Ångström) for $[Co_1(EtOH)_1]^+$, given for the C_2H_5OH (left) and C_2H_5 & OH motif (right) for $M = 3$, calculated at the BPW91/6-311+g(d,p) level.

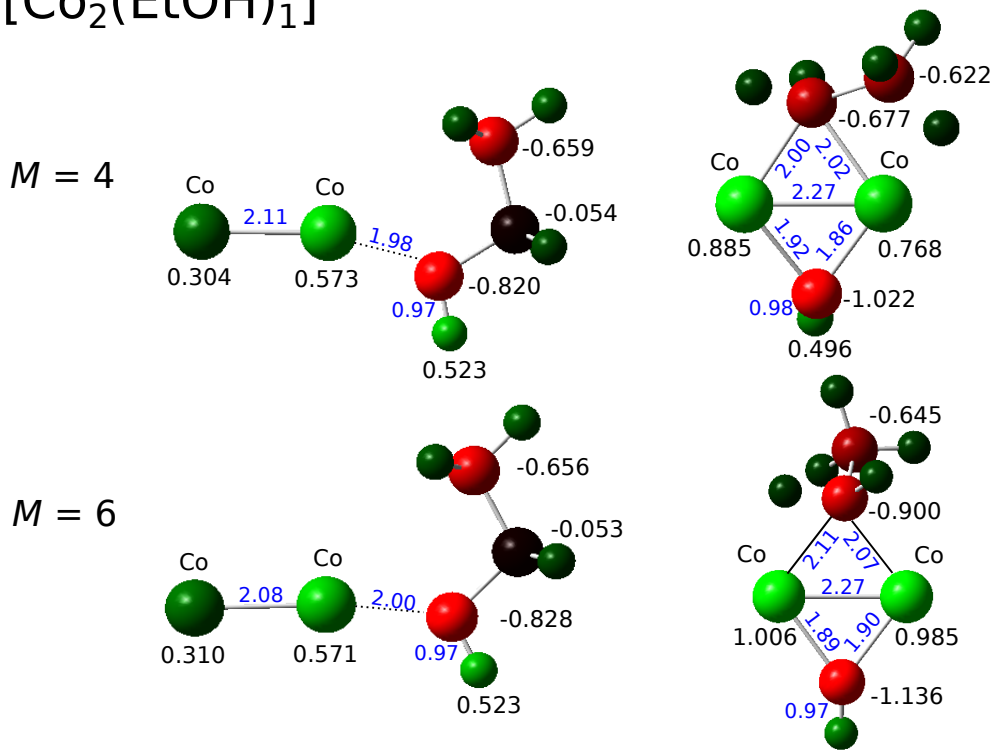

Figure S 7 Charge distribution from NBO calculations (positive: green; negative: red) and atomic distances (blue; in Ångström) for $[Co_2(EtOH)_1]^+$, given for the C_2H_5OH (left) and C_2H_5 & OH motif (right) for $M = 4$ (top) and $M = 6$ (bottom), calculated at the BPW91/6-311+g(d,p) level.

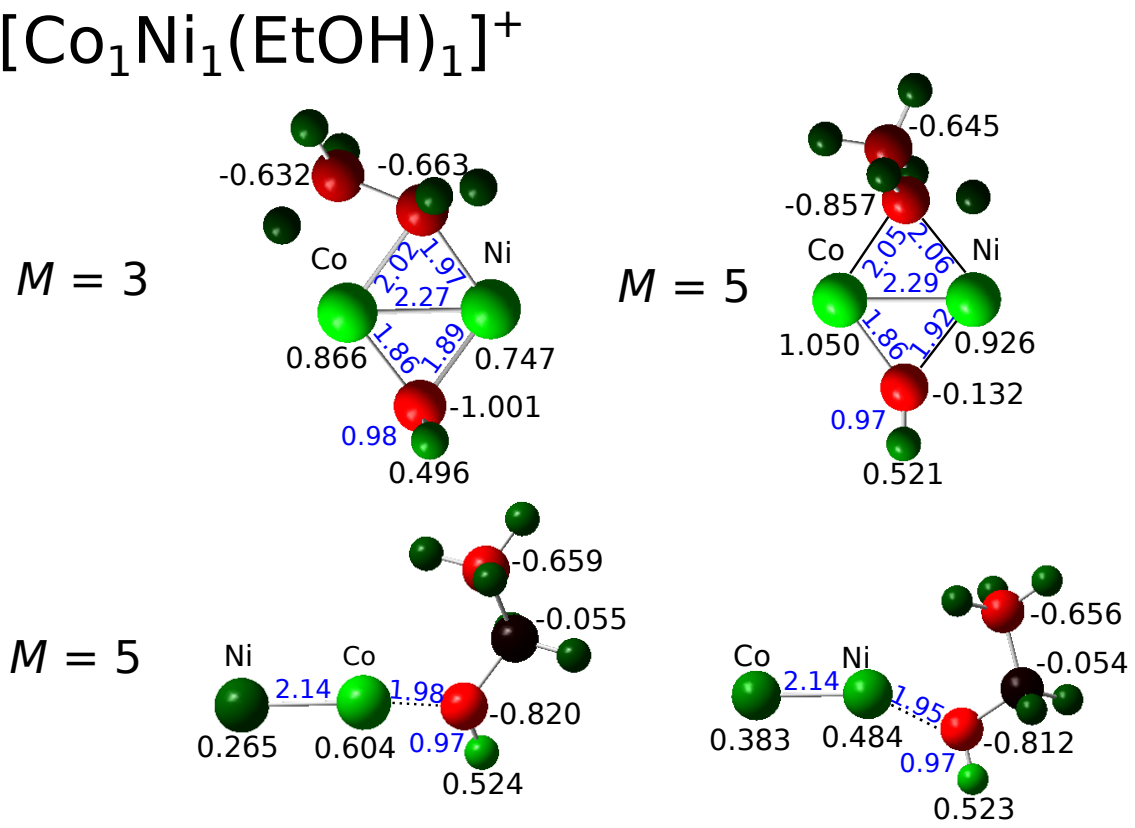

Figure S 8 Charge distribution from NBO calculations (positive: green; negative: red) and atomic distances (blue; in Ångström) for $[Co_1Ni_1(EtOH)_1]^+$, given for the C_2H_5 & OH motif (top) in $M = 3$ (left) and $M = 5$ (right) as well as the geometries #1 (left) and #2 (right) of the C_2H_5OH motif (bottom) with $M = 5$, calculated at the BPW91/6-311+g(d,p) level.

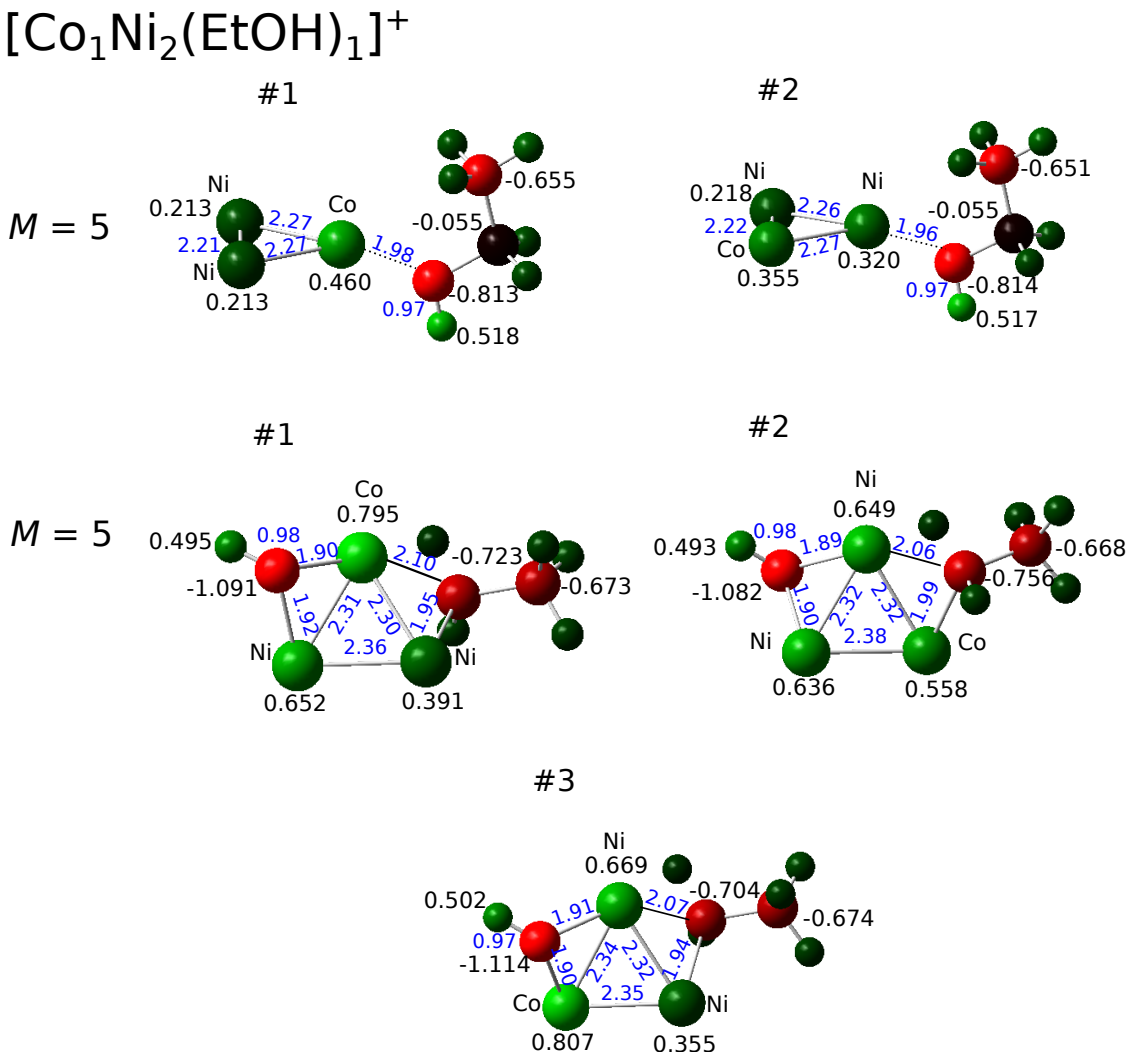

Figure S 9 Charge distribution from NBO calculations (positive: green; negative: red) and atomic distances (blue; in Ångström) of the $[Co_1Ni_2(EtOH)_1]^+$ cluster, top: C_2H_5OH motif, middle and bottom: C_2H_5 & OH motif with indicated geometry number; all in the multiplicity $M = 5$, calculated at the BPW91/6-311+g(d,p) level.

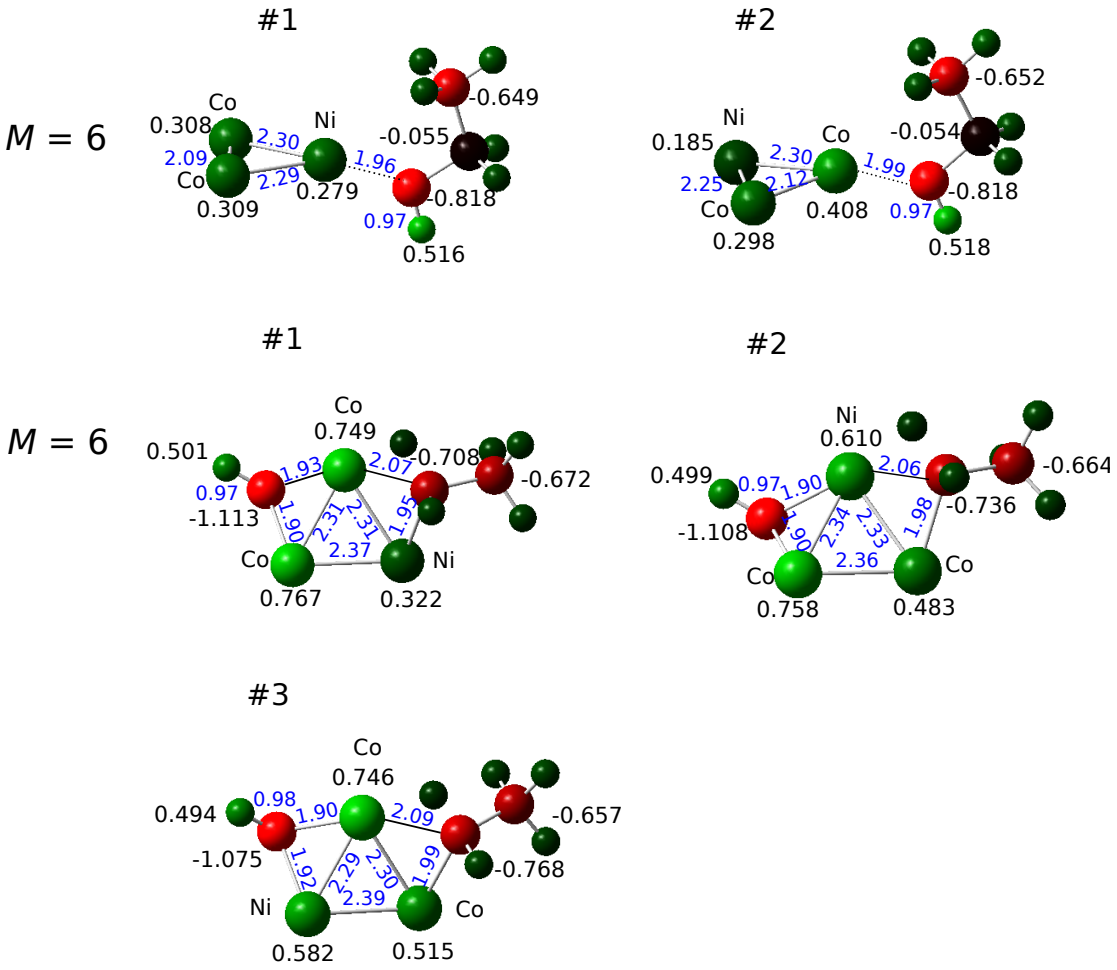

Figure S 10 Charge distribution from NBO calculations (positive: green; negative: red) and atomic distances (blue; in Ångström) of the $[Co_2Ni_1(EtOH)_1]^+$ cluster, top: C_2H_5OH motif, middle and bottom: C_2H_5 & OH motif with indicated geometry number; all in the multiplicity $M = 6$, calculated at the BPW91/6-311+g(d,p) level.