Electronic Supplementary Information

Comparative synthetic, magnetic and theoretical study of functional M_4Cl_4 cubane-type Co(II) and Ni(II) complexes

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Table S1. Crystallographic data and refinement details for **1** and **2**.

Compound reference	**1**	**2**
CCDC	964328	964329
Chemical formula	$C_{44}H_{60}Cl_8Co_4N_4O_4S_4$	$C_{44}H_{60}Cl_8Ni_4N_4O_4S_4$
Molar mass	1356.52	1355.64
Crystal system	tetragonal	tetragonal
a, Å	19.2769(8)	19.091(1)
b, Å	19.2769(8)	19.091(1)
c, Å	18.5886(8)	18.729(1)
α, °	90.00	90.00
β, °	90.00	90.00
γ, °	90.00	90.00
V, Å^3	6907.5(5)	6826.5(8)
T, K	173(2)	173(2)
Space group	$I4_1/a$	$I4_1/a$
Z	4	4
μ, mm^{-1}	1.410	1.558
Reflections measured	14447	39794
Independent reflections	5026	3351
R_{int}	0.0268	0.0261
R_1 values ($I > 2\sigma(I)$)	0.0451	0.0546
$wR(F^2)$ values ($I > 2\sigma(I)$)	0.1184	0.1257
R_1 values (all data)	0.0613	0.0623
$wR(F^2)$ values (all data)	0.1284	0.1314

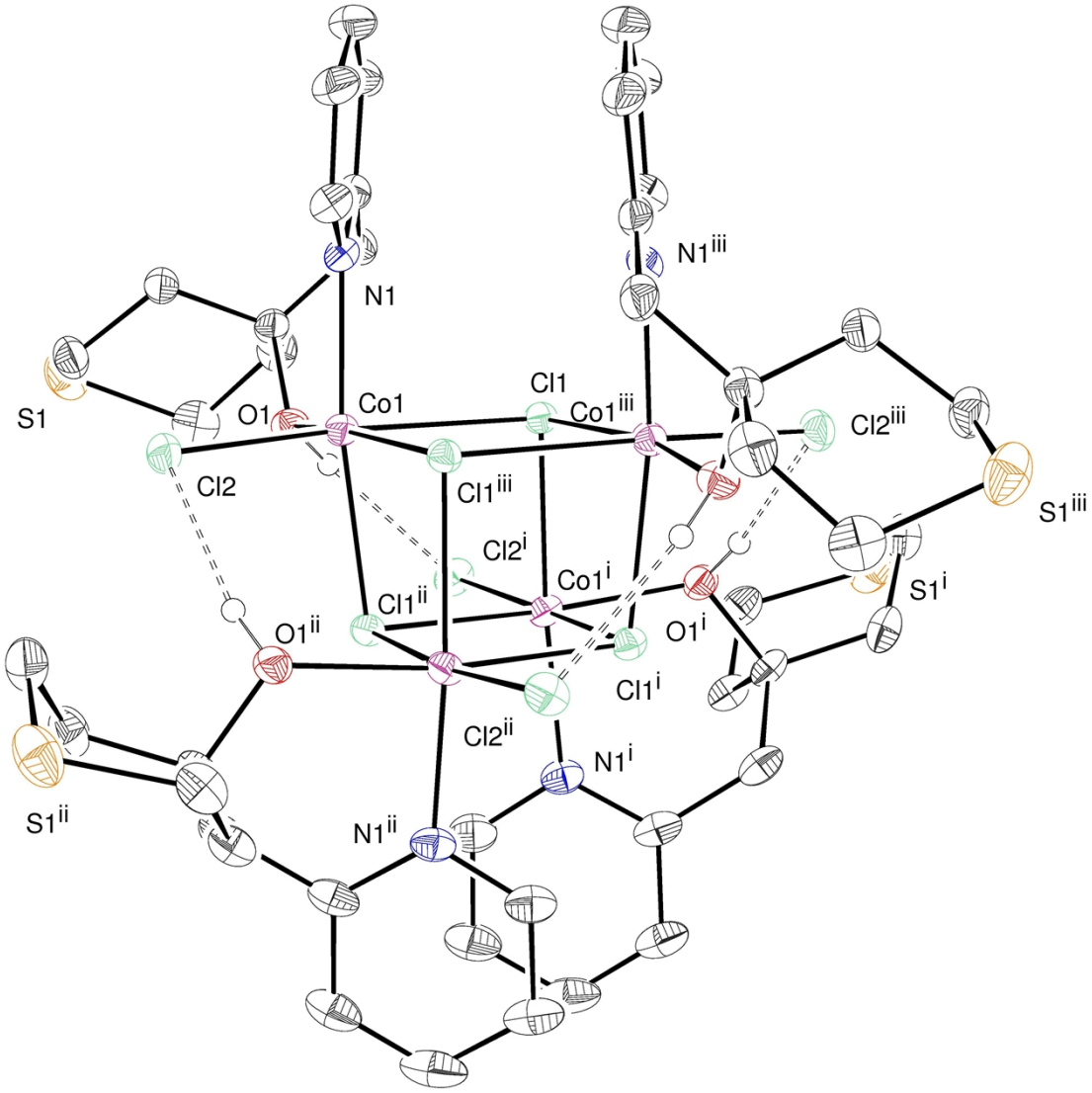

Figure S1. ORTEP of the structure **1** with complete labeling scheme of the heteroatoms. Ellipsoids probability: 40%. Symmetry operations generating equivalent atoms: i = -x, -y+1/2 z, ii = -y+1/4, x+1/4, -z+1/4; iii = y+3/4, -x+1/4, -z+1/4. Hydrogen atoms, except those from the OH functional groups, are omitted for clarity.

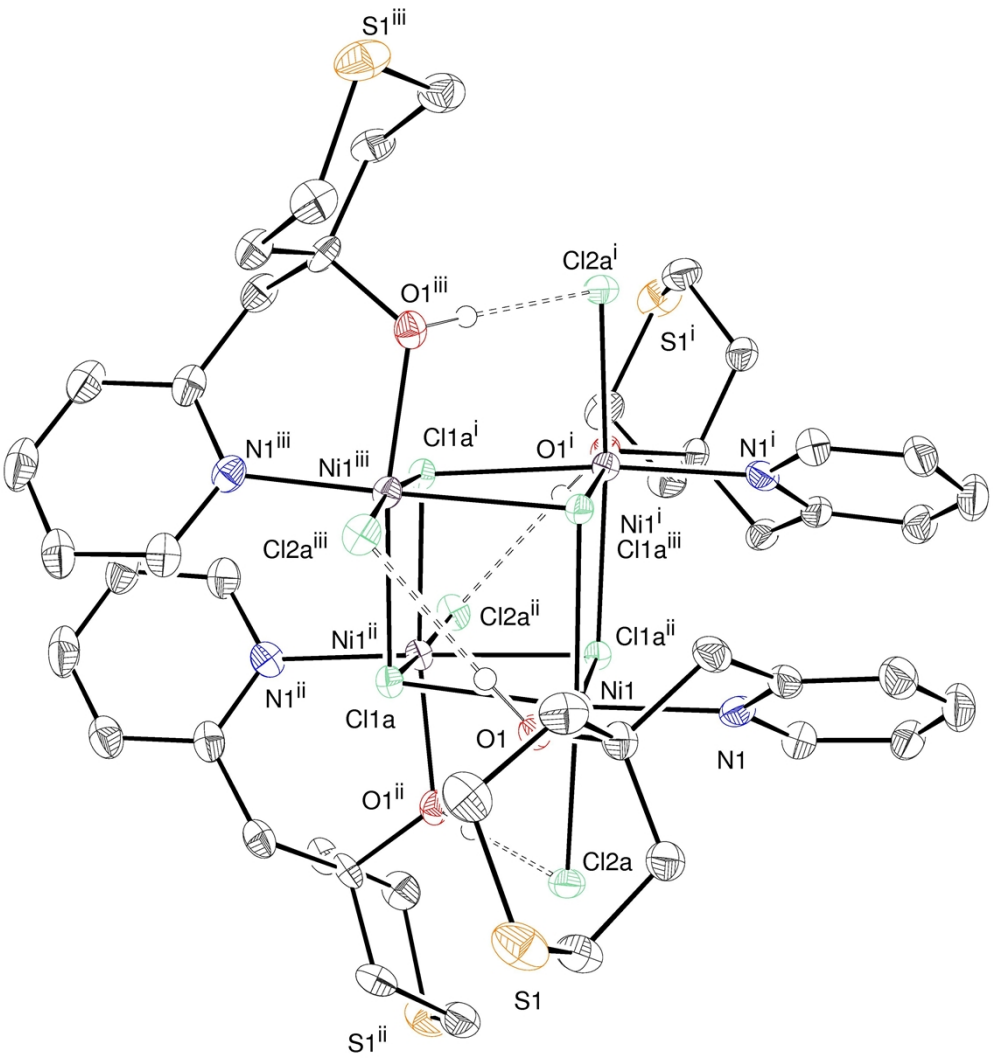

Figure S2. ORTEP of the structure **2** with complete labeling scheme of the heteroatoms. Ellipsoids probability: 40%. Symmetry operations generating equivalent atoms: i = -x, -y+1/2 z, ii = -y+1/4, x+1/4, -z+1/4; iii = y+3/4, -x+1/4, -z+1/4. Hydrogen atoms, except those from the OH functional groups, are omitted for clarity.

Table S2. Cartesian coordinates (in Å), total energies (in kcal·mol^{-1}) and NImag of the stationary points obtained for the optimized high-spin structures [M(μ_3-Cl)Cl(**HL·S**)]$_4$ (**1**$_{DFT:}$ M = Co; **2**$_{DFT}$: M = Ni) and the ground-state structures [MCl$_2$(**HL·S**)] (**1'**$_{DFT}$ and **2'**$_{DFT}$) at the COSMO/ZORA-(U)BP86-D3/TZ2P level of theory.[a]

1$_{DFT}$ (S_{HS} = 6): –17243.20 (0)

C	0.111482	-1.856194	4.043599
H	1.024976	-2.025610	3.480043
C	0.117321	-1.796916	5.430162
H	1.052813	-1.913882	5.972695
C	-1.091897	-1.582607	6.090662
H	-1.132412	-1.523480	7.177190
C	-2.252707	-1.455660	5.332898
H	-3.217674	-1.306611	5.814909
C	-2.192892	-1.522122	3.935825
C	-3.453002	-1.396870	3.121446
H	-3.466440	-0.415197	2.625496
H	-4.309735	-1.428117	3.806148
C	-3.659951	-2.457221	2.018626
C	-5.101551	-2.354823	1.491838
H	-5.786773	-2.586142	2.320130
H	-5.286623	-1.312852	1.185383
C	-5.386992	-3.278229	0.307410
H	-4.743630	-3.025711	-0.546147
H	-6.431048	-3.180711	-0.013387
C	-3.450469	-4.926124	1.399621
H	-3.211139	-5.923697	1.787419
H	-2.753248	-4.694163	0.583924
C	-3.317829	-3.873914	2.498158
H	-2.273047	-3.882053	2.841676
H	-3.962932	-4.117421	3.355685
N	-1.007790	-1.709941	3.302882
O	-2.743521	-2.184533	0.918831
S	-5.155294	-5.051022	0.726840
Cl	-1.490490	0.712133	1.242398
Cl	0.150229	-3.892359	1.129091
Co	-0.751775	-1.728200	1.238653
H	-3.144177	-1.518101	0.283476
C	-0.111482	1.856194	4.043599
H	-1.024976	2.025610	3.480043
C	-0.117321	1.796916	5.430162
H	-1.052813	1.913882	5.972695
C	1.091897	1.582607	6.090662
H	1.132412	1.523480	7.177190
C	2.252707	1.455660	5.332898
H	3.217674	1.306611	5.814909
C	2.192892	1.522122	3.935825
C	3.453002	1.396870	3.121446
H	3.466440	0.415197	2.625496
H	4.309735	1.428117	3.806148
C	3.659951	2.457221	2.018626
C	5.101551	2.354823	1.491838
H	5.786773	2.586142	2.320130
H	5.286623	1.312852	1.185383
C	5.386992	3.278229	0.307410
H	4.743630	3.025711	-0.546147
H	6.431048	3.180711	-0.013387

C	3.450469	4.926124	1.399621
H	3.211139	5.923697	1.787419
H	2.753248	4.694163	0.583924
C	3.317829	3.873914	2.498158
H	2.273047	3.882053	2.841676
H	3.962932	4.117421	3.355685
N	1.007790	1.709941	3.302882
O	2.743521	2.184533	0.918831
S	5.155294	5.051022	0.726840
Cl	1.490490	-0.712133	1.242398
Cl	-0.150229	3.892359	1.129091
Co	0.751775	1.728200	1.238653
H	3.144177	1.518101	0.283476
C	-1.854609	-0.110694	-4.043792
H	-2.023412	-1.024459	-3.480529
C	-1.794956	-0.116188	-5.430364
H	-1.910622	-1.051829	-5.972844
C	-1.581799	1.093327	-6.090583
H	-1.522438	1.134158	-7.177091
C	-1.456228	2.254158	-5.332622
H	-1.308317	3.219389	-5.814457
C	-1.522818	2.194029	-3.935581
C	-1.399300	3.454280	-3.121192
H	-0.417638	3.469114	-2.625213
H	-1.432265	4.310953	-3.805873
C	-2.459941	3.659265	-2.018343
C	-2.360219	5.101088	-1.491665
H	-2.591898	5.785753	-2.320256
H	-1.318784	5.287820	-1.184443
C	-3.285068	5.385071	-0.308010
H	-3.032657	4.741772	0.545628
H	-3.189392	6.429180	0.013231
C	-4.928492	3.445518	-1.399402
H	-5.925401	3.203090	-1.786861
H	-4.695081	2.750095	-0.582586
C	-3.875914	3.314178	-2.497638
H	-3.882024	2.269157	-2.840400
H	-4.120507	3.958344	-3.355536
N	-1.709556	1.008586	-3.302912
O	-2.184871	2.743424	-0.918695
S	-5.057054	5.151004	-0.728900
Cl	0.712115	1.491329	-1.242219
Cl	-3.891341	-0.151020	-1.130775
Co	-1.727698	0.751918	-1.238654
H	-1.517500	3.144800	-0.285003
C	1.854609	0.110694	-4.043792
H	2.023412	1.024459	-3.480529
C	1.794956	0.116188	-5.430364
H	1.910622	1.051829	-5.972844
C	1.581799	-1.093327	-6.090583
H	1.522438	-1.134158	-7.177091
C	1.456228	-2.254158	-5.332622
H	1.308317	-3.219389	-5.814457
C	1.522818	-2.194029	-3.935581
C	1.399300	-3.454280	-3.121192
H	0.417638	-3.469114	-2.625213
H	1.432265	-4.310953	-3.805873
C	2.459941	-3.659265	-2.018343
C	2.360219	-5.101088	-1.491665

H	2.591898	-5.785753	-2.320256
H	1.318784	-5.287820	-1.184443
C	3.285068	-5.385071	-0.308010
H	3.032657	-4.741772	0.545628
H	3.189392	-6.429180	0.013231
C	4.928492	-3.445518	-1.399402
H	5.925401	-3.203090	-1.786861
H	4.695081	-2.750095	-0.582586
C	3.875914	-3.314178	-2.497638
H	3.882024	-2.269157	-2.840400
H	4.120507	-3.958344	-3.355536
N	1.709556	-1.008586	-3.302912
O	2.184871	-2.743424	-0.918695
S	5.057054	-5.151004	-0.728900
Cl	-0.712115	-1.491329	-1.242219
Cl	3.891341	0.151020	-1.130775
Co	1.727698	-0.751918	-1.238654
H	1.517500	-3.144800	-0.285003

2$_{DFT}$ (S_{HS} = 4): –17016.36 (0)

Ni	-0.780760	-1.646140	1.240659
Cl	-0.711339	-1.468624	-1.209597
Cl	0.085323	-3.841833	1.104438
N	-0.976694	-1.664899	3.258111
O	-2.738449	-2.170620	0.884745
C	-3.644041	-2.432950	1.994693
C	-3.427782	-1.368800	3.092582
H	-3.446784	-0.387630	2.595996
H	-4.277983	-1.399901	3.785128
C	-2.161555	-1.498164	3.896821
C	-2.213371	-1.465975	5.295484
H	-3.176669	-1.331504	5.784664
C	-1.049423	-1.608877	6.044924
H	-1.085785	-1.576030	7.132606
C	0.156676	-1.807905	5.374657
H	1.094507	-1.940537	5.909417
C	0.145887	-1.834392	3.987078
H	1.054424	-1.996894	3.414546
C	-5.089249	-2.324069	1.476480
H	-5.770258	-2.552120	2.309213
H	-5.270649	-1.281764	1.169126
C	-5.383570	-3.247277	0.294232
H	-4.741785	-2.996925	-0.561157
H	-6.428749	-3.146030	-0.021972
C	-3.450658	-4.903995	1.384608
H	-3.217448	-5.901963	1.775037
H	-2.752746	-4.677739	0.568385
C	-3.309193	-3.849250	2.479676
H	-2.263420	-3.863677	2.819968
H	-3.954210	-4.085433	3.339416
S	-5.157642	-5.020524	0.714923
H	-3.131214	-1.469635	0.279313
Ni	-1.646033	0.780511	-1.240664
Cl	-1.468646	0.711332	1.209729
Cl	-3.842024	-0.085728	-1.105332
N	-1.664189	0.976682	-3.258093
O	-2.170724	2.737997	-0.884309
C	-2.433202	3.643465	-1.994301

C	-1.368622	3.427661	-3.091867
H	-0.387608	3.446757	-2.595007
H	-1.399582	4.278027	-3.784229
C	-1.497537	2.161665	-3.896507
C	-1.464936	2.213830	-5.295104
H	-1.330616	3.177264	-5.784031
C	-1.607439	1.050021	-6.044819
H	-1.574406	1.086600	-7.132495
C	-1.806385	-0.156208	-5.374854
H	-1.938870	-1.093918	-5.909853
C	-1.833165	-0.145743	-3.987300
H	-1.995387	-1.054475	-3.415077
C	-2.324936	5.088679	-1.475971
H	-2.551567	5.769710	-2.309036
H	-1.282955	5.269772	-1.167390
C	-3.249773	5.383415	-0.295280
H	-3.000920	4.741737	0.560597
H	-3.148935	6.428587	0.021120
C	-4.904389	3.449821	-1.385300
H	-5.902018	3.215023	-1.775684
H	-4.677889	2.753456	-0.567832
C	-3.849107	3.307522	-2.479553
H	-3.862593	2.261253	-2.818360
H	-4.085241	3.951335	-3.340182
S	-5.022131	5.157628	-0.718405
H	-1.469876	3.130875	-0.278810
Ni	1.646033	-0.780511	-1.240664
Cl	1.468646	-0.711332	1.209729
Cl	3.842024	0.085728	-1.105332
N	1.664189	-0.976682	-3.258093
O	2.170724	-2.737997	-0.884309
C	2.433202	-3.643465	-1.994301
C	1.368622	-3.427661	-3.091867
H	0.387608	-3.446757	-2.595007
H	1.399582	-4.278027	-3.784229
C	1.497537	-2.161665	-3.896507
C	1.464936	-2.213830	-5.295104
H	1.330616	-3.177264	-5.784031
C	1.607439	-1.050021	-6.044819
H	1.574406	-1.086600	-7.132495
C	1.806385	0.156208	-5.374854
H	1.938870	1.093918	-5.909853
C	1.833165	0.145743	-3.987300
H	1.995387	1.054475	-3.415077
C	2.324936	-5.088679	-1.475971
H	2.551567	-5.769710	-2.309036
H	1.282955	-5.269772	-1.167390
C	3.249773	-5.383415	-0.295280
H	3.000920	-4.741737	0.560597
H	3.148935	-6.428587	0.021120
C	4.904389	-3.449821	-1.385300
H	5.902018	-3.215023	-1.775684
H	4.677889	-2.753456	-0.567832
C	3.849107	-3.307522	-2.479553
H	3.862593	-2.261253	-2.818360
H	4.085241	-3.951335	-3.340182
S	5.022131	-5.157628	-0.718405
H	1.469876	-3.130875	-0.278810
Ni	0.780760	1.646140	1.240659

Cl	0.711339	1.468624	-1.209597
Cl	-0.085323	3.841833	1.104438
N	0.976694	1.664899	3.258111
O	2.738449	2.170620	0.884745
C	3.644041	2.432950	1.994693
C	3.427782	1.368800	3.092582
H	3.446784	0.387630	2.595996
H	4.277983	1.399901	3.785128
C	2.161555	1.498164	3.896821
C	2.213371	1.465975	5.295484
H	3.176669	1.331504	5.784664
C	1.049423	1.608877	6.044924
H	1.085785	1.576030	7.132606
C	-0.156676	1.807905	5.374657
H	-1.094507	1.940537	5.909417
C	-0.145887	1.834392	3.987078
H	-1.054424	1.996894	3.414546
C	5.089249	2.324069	1.476480
H	5.770258	2.552120	2.309213
H	5.270649	1.281764	1.169126
C	5.383570	3.247277	0.294232
H	4.741785	2.996925	-0.561157
H	6.428749	3.146030	-0.021972
C	3.450658	4.903995	1.384608
H	3.217448	5.901963	1.775037
H	2.752746	4.677739	0.568385
C	3.309193	3.849250	2.479676
H	2.263420	3.863677	2.819968
H	3.954210	4.085433	3.339416
S	5.157642	5.020524	0.714923
H	3.131214	1.469635	0.279313

1'$_{DFT}$ (*S*' = 3/2): –4294.75 (0)

C	9.862393	12.834963	6.343250
H	10.776927	12.732736	5.763045
C	9.870720	12.854198	7.730813
H	10.813817	12.778081	8.266358
C	8.653153	12.964748	8.402919
H	8.618583	12.976207	9.490772
C	7.475868	13.054157	7.661341
H	6.509756	13.135338	8.155671
C	7.528920	13.036509	6.266983
C	6.281075	13.129248	5.428510
H	6.322444	14.043628	4.815912
H	5.419018	13.229468	6.098058
C	6.018536	11.941569	4.469875
C	4.574425	12.022427	3.956813
H	3.904055	11.965403	4.826052
H	4.424858	13.014336	3.498582
C	4.203430	10.930476	2.952712
H	4.830456	10.984079	2.051855
H	3.157010	11.037227	2.644414
C	6.106217	9.391390	4.198028
H	6.338889	8.458244	4.723878
H	6.738969	9.450152	3.302395
C	6.359281	10.592394	5.107864
H	7.424969	10.597233	5.386230
H	5.777693	10.501247	6.037393

N	8.720959	12.925148	5.625638
O	6.923521	12.059153	3.299356
S	4.354118	9.251279	3.673464
Co	8.809612	12.783086	3.648723
Cl	10.408885	11.375888	3.085095
Cl	8.652696	14.731919	2.601069
H	6.509591	12.656358	2.643541

2'$_{DFT}$ (S' = 0): –4231.86 (0)

Ni	8.426821	13.014966	3.644795
Cl	8.001668	12.876500	1.499256
N	8.643486	12.925701	5.514098
O	7.194494	11.525969	3.843158
C	5.934586	11.747936	4.609202
C	6.210971	12.926883	5.560772
H	6.210840	13.855760	4.970459
H	5.388077	12.988709	6.281708
C	7.524173	12.811754	6.277746
C	7.624414	12.588273	7.649681
H	6.713115	12.502656	8.238090
C	8.880241	12.483942	8.246283
H	8.967800	12.308215	9.316736
C	10.017386	12.609966	7.449311
H	11.018383	12.536440	7.867299
C	9.863138	12.832866	6.087347
H	10.710455	12.947134	5.418667
C	4.818619	12.123570	3.628852
H	3.920570	12.360395	4.217131
H	5.126590	13.039143	3.099365
C	4.492962	11.034259	2.605013
H	5.345938	10.837546	1.934221
H	3.659921	11.350994	1.967349
C	5.433620	9.242040	4.474011
H	5.230683	8.345304	5.070916
H	6.317596	9.041117	3.852068
C	5.667188	10.450837	5.380029
H	6.531177	10.253230	6.033654
H	4.788727	10.610682	6.022945
S	3.973974	9.457148	3.381558
H	6.972240	11.336460	2.901052
Cl	9.800927	14.660367	3.441861

[a] Total energies are relative to ADF's basic atoms and NImag is the number of imaginary frequencies (in parentheses).