Electronic Supplementary Information (ESI)

Tetranuclear Ni(II) and Co(II) Schiff-base complexes with an M_4O_6 defective dicubane-like core: zero-field SMM behavior in the cobalt analogue

Ivan Nemec, Radovan Herchel, Marek Machata and Zdeněk Trávníček*

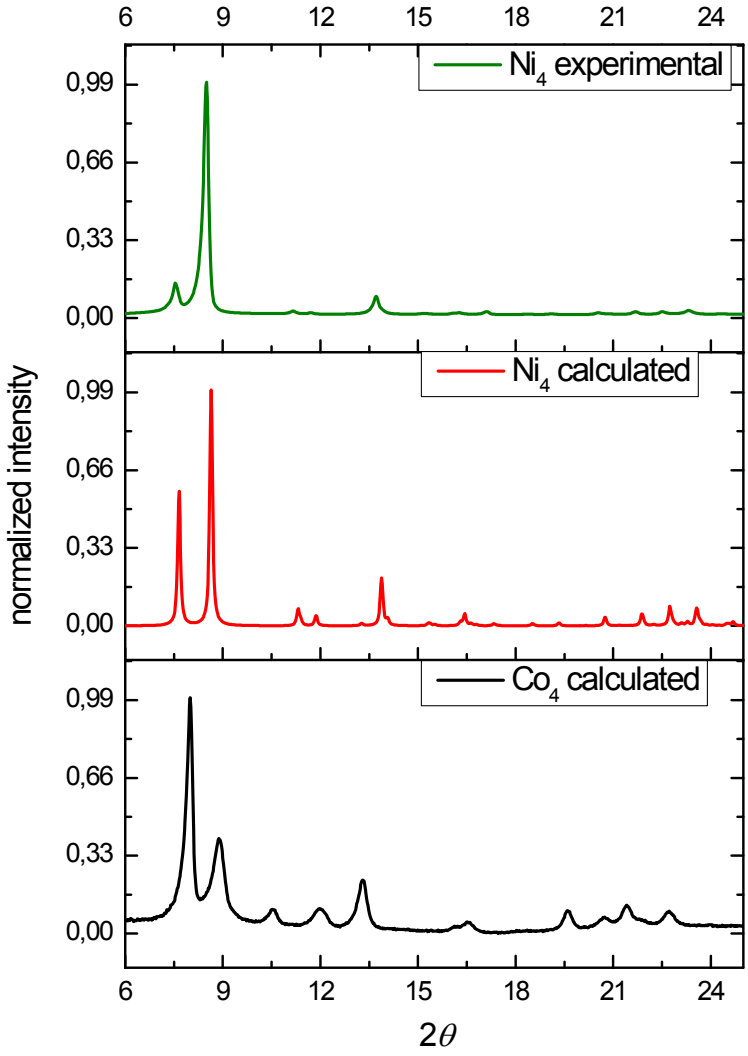


Fig. S1 Comparison of the calculated powder diffraction pattern for **1** (red line) with the experimental diffraction patterns collected for **1** (green) and **2** (black). *Note*: temperature of the single-crystal measurement was 150 K, while temperature of the powder diffraction experiments was 298 K.

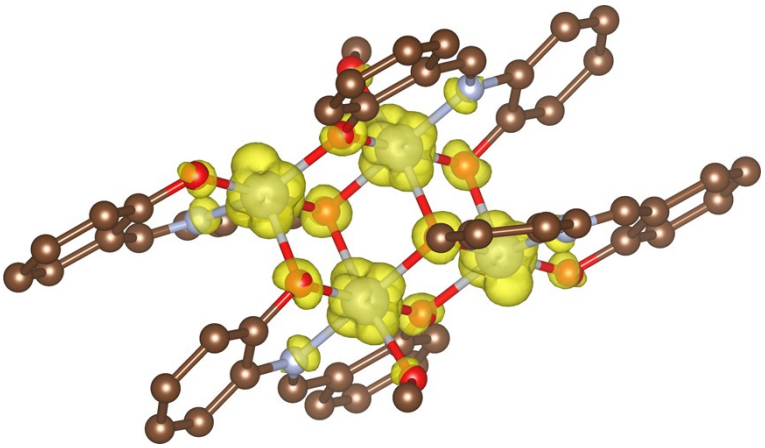


Fig. S2 The calculated the isodensity surfaces of the HS spin states using B3LYP/ZORA/def2-TZVP(-f) for **1**. The spin density is represented by yellow surface with the cutoff values of 0.01 e·boh^{-3}. Hydrogen atoms were omitted for clarity.

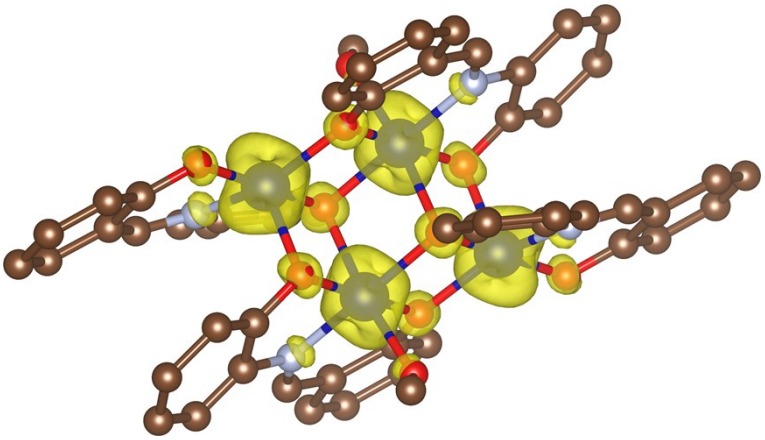


Fig. S3 The calculated the isodensity surfaces of the HS spin states using B3LYP/ZORA/def2-TZVP(-f) for **2**. The spin density is represented by yellow surface with the cutoff values of 0.01 e·boh^{-3}. Hydrogen atoms were omitted for clarity.

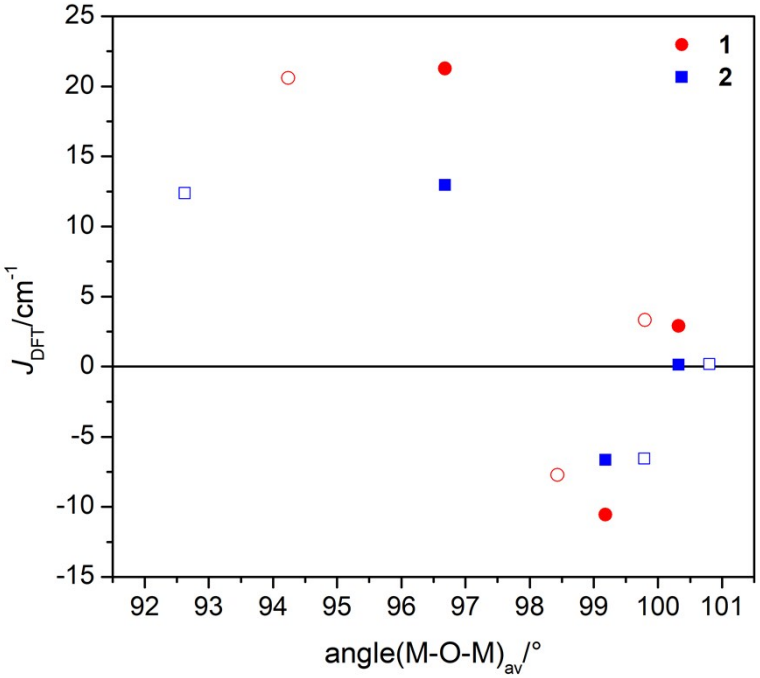


Fig. S4 The DFT derived J_{ab}-parameters for compounds **1** and **2** *vs*. average M_a-O-M_b angles. Full symbols calculated for X-ray derived molecular geometries, empty symbols for BP86-optimized geometries.

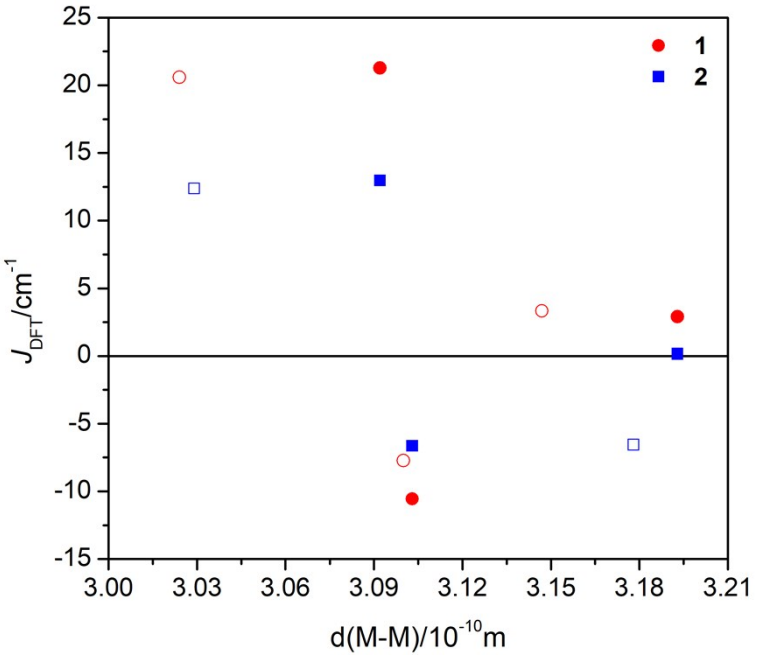
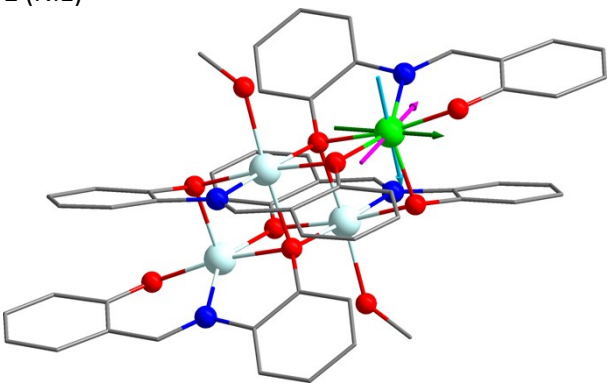


Fig. S5 The DFT derived J_{ab}-parameters for compounds **1** and **2** *vs*. interatomic distance d(M_a···M_b). Full symbols calculated for X-ray derived molecular geometries, empty symbols for BP86-optimized geometries.

1 (Ni1)



1 (Ni2)

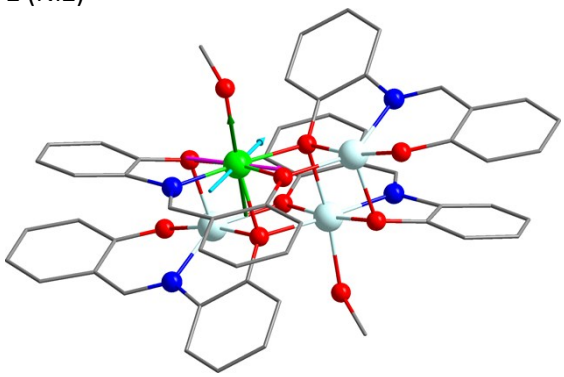
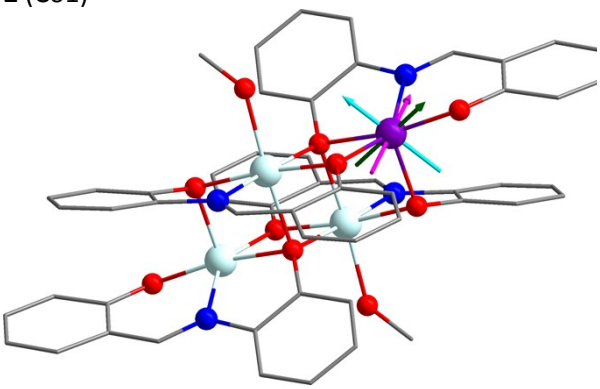


Fig. S6 The CASSCF/NEVPT2 principal axes of ZFS *D*-tensors (DX - magenta, DY – dark green, DZ – cyan) visualized together with the molecular structure $[NiZn_3(L)_4(CH_3OH)_2]$ derived from X-ray data of compound **1.** Hydrogen atoms were omitted for clarity.

2 (Co1)



2 (Co2)

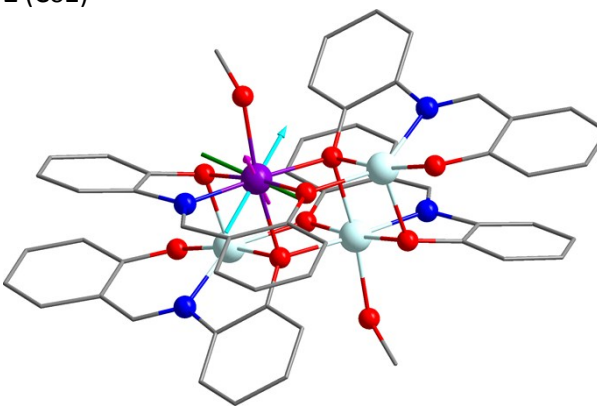


Fig. S7 The CASSCF/NEVPT2 principal axes of ZFS *D*-tensors (DX - magenta, DY – dark green, DZ – cyan) visualized together with the molecular structure $[CoZn_3(L)_4(CH_3OH)_2]$ derived from X-ray data of compound **1.** Hydrogen atoms were omitted for clarity.

Table S1. Basic crystallographic data for compound **1**

	1
Formula	$C_{54}H_{44}N_4Ni_4O_{10}$
M (g·mol^{-1})	1143.74
Crystal system	Triclinic
Space group	$P\overline{1}$
λ (Å)	0.71073
a (Å)	8.4860(4)
b (Å)	12.0008(7)
c (Å)	12.9636(7)
α (°)	112.276(5)
β (°)	97.062(4)
γ (°)	108.048(4)
V (Å^3)	1117.36(11)
Z	2
T(K)	150
ρ_{calcd} (g·cm^{-3})	1.700
μ (mm^{-1})	1.730
Data/restraints/parameters	3932/9/345
Goodness-of-fit	0.975
R_{int}/R_σ	0.0407/0.0523
$R_1{}^a$ [I > 2σ(I)]/R_1 (all)	0.0340/0.0505
$wR_2{}^b$ [I > 2σ(I)]/wR_2 (all)	0.0713/0.0767
Maximum peak and hole (e A^{-3})	0.568 and -0.669
CCDC number	1443521

Table S2. Energy levels (cm^{-1}) of ligand field multiplets in zero magnetic field derived from CASSCF/NEVPT2/ZORA/def2-TZVP(-f) calculations for **1-2** using molecular geometries from X-ray data.

	1 (Ni1)	**1** (Ni2)	**2** (Co1)	**2** (Co2)
0:	0.0000	0.0000	0.0000	0.0000
1:	19.9124	5.5776	0.0000	0.0000
2:	33.6048	12.2600	108.6404	160.1502
3:	4649.5372	8828.6879	108.6404	160.1502
4:	4749.4851	8939.8416	1021.7460	677.9864
5:	4939.7037	9033.2666	1021.7460	677.9864
6:	5931.1779	10147.2092	1169.4523	951.2741
7:	5972.9875	10174.4712	1169.4523	951.2741
8:	6105.5744	10259.1703	2242.9614	1370.9282
9:	10524.9791	13091.6143	2242.9614	1370.9282
10:	10581.7591	13228.5985	2320.1414	1491.2767
11:	10860.2768	13236.7928	2320.1414	1491.2767
12:	11403.8269	14759.4480	4725.0934	6402.4954
13:	11440.4924	16427.3591	4725.0934	6402.4954
14:	11662.9975	16966.0539	4827.1980	8942.2090
15:	13050.2594	16987.9052	4827.1980	8942.2090
16:	14295.3390	17093.8339	8666.3008	8999.3739
17:	14355.0085	18710.5261	8666.3008	8999.3739

18:	14509.6350	18907.0724	8697.5106	11048.8589
19:	15165.1431	18971.0673	8697.5106	11048.8589
20:	15372.8663	19843.3780	9033.4350	11490.1681
21:	15384.5953	19884.9074	9033.4350	11490.1681
22:	16426.4193	20010.0515	10464.3633	11556.4711
23:	20334.1239	24648.8873	10464.3633	11556.4711
24:	21024.0061	25696.2082	10577.2027	12813.1363
25:	23639.1967	28348.4117	10577.2027	12813.1363
26:	23779.2594	29031.0805	14061.9996	12907.0795
27:	23809.2132	29166.4345	14061.9996	12907.0795
28:	25190.4965	29231.6830	15539.7321	15861.9516
29:	26480.8494	29687.3520	15539.7321	15861.9516
30:	26930.5434	30743.2555	16005.7541	17221.9311
31:	27028.6116	30786.4542	16005.7541	17221.9311
32:	27320.3165	30875.7524	16166.3072	18513.7906
33:	28286.1938	31041.2147	16166.3072	18513.7906
34:	28357.8953	32302.7354	16211.2479	19023.2684
35:	28478.1506	32324.3565	16211.2479	19023.2684
36:	29421.9424	32413.1454	18651.6918	19677.5032
37:	31779.2298	34813.2335	18651.6918	19677.5032
38:	32824.6376	34929.4847	19574.8707	21401.9660
39:	34707.7461	40441.7819	19574.8707	21401.9660
40:	35213.6933	40781.0836	19665.0612	22188.0003
41:	35664.5122	41476.1374	19665.0612	22188.0003
42:	36634.3485	42281.2755	19714.4345	22665.9791
43:	36985.7438	42592.1095	19714.4345	22665.9791
44:	62162.2165	67092.0313	19834.9353	22937.5653
45:			19834.9353	22937.5653
46:			20087.5457	23052.5231
47:			20087.5457	23052.5231
48:			21898.2344	23258.6506
49:			21898.2344	23258.6506
50:			22175.6480	23505.0438
51:			22175.6480	23505.0438
52:			22242.4870	23677.2247
53:			22242.4870	23677.2248
54:			22639.2923	24368.4840
55:			22639.2923	24368.4840
56:			23057.5519	24590.9532
57:			23057.5519	24590.9532
58:			23265.9135	26812.1502
59:			23265.9135	26812.1502
60:			25946.2395	27335.2051
61:			25946.2395	27335.2051
62:			26037.6005	27403.8286
63:			26037.6005	27403.8286
64:			26847.9900	29310.9376
65:			26847.9900	29310.9376
66:			27514.6632	29806.4614
67:			27514.6632	29806.4614
68:			28189.5221	30297.9765
69:			28189.5221	30297.9765
70:			28886.9392	31280.8307
71:			28886.9392	31280.8307
72:			29754.6857	32548.9823
73:			29754.6857	32548.9823
74:			30809.8497	33133.7949

75:			30809.8497	33133.7949
76:			31502.7698	33502.4233
77:			31502.7698	33502.4233
78:			32264.0568	34712.5924
79:			32264.0568	34712.5924
80:			32428.3719	36374.4375
81:			32428.3719	36374.4375
82:			32707.9534	36975.0474
83:			32707.9534	36975.0474
84:			33429.3408	37200.7597
85:			33429.3408	37200.7597
86:			34028.1827	38764.8918
87:			34028.1827	38764.8918
88:			34522.0079	39675.9500
89:			34522.0079	39675.9500
90:			35688.3771	40652.8072
91:			35688.3771	40652.8072
92:			36047.9359	40878.4091
93:			36047.9359	40878.4091
94:			36767.2083	41252.1356
95:			36767.2083	41252.1356
96:			41431.2846	42910.1222
97:			41431.2846	42910.1222
98:			42701.5538	44707.8409
99:			42701.5538	44707.8409
100:			42912.6509	45332.6626
101:			42912.6509	45332.6626
102:			44954.6833	46870.1898
103:			44954.6833	46870.1898
104:			45055.4289	47906.3039
105:			45055.4289	47906.3039
106:			45511.2530	48209.4437
107:			45511.2530	48209.4437
108:			45691.6028	48312.0540
109:			45691.6028	48312.0540
110:			61431.8172	65552.8222
111:			61431.8172	65552.8222
112:			62913.8331	67084.0735
113:			62913.8331	67084.0735
114:			65211.0795	68213.7704
115:			65211.0795	68213.7704
116:			66403.0738	69429.1413
117:			66403.0738	69429.1413
118:			67567.4404	69830.5383
119:			67567.4404	69830.5383

Table S3. Individual contributions to *D*-tensor for **1** and **2** using molecular geometries from X-ray data calculated by CASSCF/NEVPT2/ZORA/def2-TZVP(-f).

		1 (Ni1)		**1** (Ni2)				**2** (Co1)		**2** (Co2)	
(2*S*+1)	Root	*D*	*E*	*D*	*E*	(2*S*+1)	Root	*D*	*E*	*D*	*E*
3	0	0.000	-0.000	-0.000	0.000	4	0	-0.000	0.000	0.000	0.000
3	1	37.865	38.849	-41.759	-1.276	4	1	37.019	37.017	39.575	35.801
3	2	31.607	-31.892	14.855	-17.637	4	2	16.778	-16.771	24.592	-20.115
3	3	-27.094	1.192	15.014	15.151	4	3	5.621	-5.627	4.316	0.734
3	4	-5.807	0.066	-0.030	0.028	4	4	-11.784	0.036	-7.567	-0.146
3	5	0.916	-0.913	-0.163	-0.098	4	5	1.087	-1.117	0.954	0.367
3	6	-0.257	0.273	0.062	-0.072	4	6	-0.392	-0.001	-0.011	-0.002
3	7	-0.020	0.003	0.009	-0.003	4	7	0.001	-0.001	0.030	-0.046
3	8	0.088	-0.090	0.015	-0.015	4	8	-0.135	0.018	0.045	0.038
3	9	0.046	0.044	-0.030	-0.002	4	9	0.054	-0.054	0.072	-0.005
1	0	-0.239	0.249	0.027	0.001	2	0	-0.067	-1.949	-4.197	1.496
1	1	-0.025	0.011	-0.001	0.001	2	1	-0.090	0.111	2.313	0.256
1	2	-7.814	-7.887	14.614	0.015	2	2	-0.002	-0.294	0.009	-0.002
1	3	-7.552	7.567	-6.570	6.545	2	3	-0.904	-1.332	-0.487	-0.003
1	4	10.860	-0.020	-5.943	-5.877	2	4	-0.350	0.339	-0.551	-0.186
1	5	0.915	-0.162	-0.004	-0.001	2	5	-0.084	0.022	-0.548	-0.179
1	6	-0.014	0.009	-0.033	-0.047	2	6	-0.706	-0.799	-0.805	0.398
1	7	0.018	0.049	-0.114	0.117	2	7	-1.350	1.185	-0.143	-0.070
1	8	0.502	-0.002	-0.031	0.051	2	8	1.502	-0.573	0.013	-0.049
1	9	-0.202	0.152	-0.040	-0.006	2	9	0.335	0.006	0.353	0.055
1	10	-0.099	-0.137	-0.302	0.145	2	10	-0.165	0.166	2.499	-0.019
1	11	-0.616	-0.216	-0.295	0.274	2	11	-0.025	0.024	0.025	0.013
1	12	-0.694	0.366	0.627	-0.150	2	12	-0.107	0.103	-0.309	0.140
1	13	1.755	0.035	-0.254	-0.424	2	13	-0.162	-0.167	-0.188	-0.256
1	14	-0.002	0.003	0.001	-0.000	2	14	-0.103	0.111	0.026	-0.017
						2	15	-0.241	0.246	-0.044	-0.000
						2	16	-0.050	-0.138	0.086	-0.031
						2	17	0.282	-0.094	0.063	-0.005
						2	18	-0.238	0.176	0.198	-0.113
						2	19	0.197	-0.214	-0.400	0.323
						2	20	-0.124	0.178	0.484	-0.064
						2	21	1.801	-0.038	-0.177	-0.002
						2	22	-0.062	-0.082	0.034	-0.080
						2	23	-0.042	0.000	0.177	0.074
						2	24	-0.135	0.046	0.083	-0.014
						2	25	0.110	-0.056	-0.232	0.085
						2	26	-0.039	-0.039	-0.000	0.010
						2	27	0.001	0.005	-0.053	0.025
						2	28	-0.167	0.175	-0.138	-0.071
						2	29	0.001	-0.000	0.104	0.028
						2	30	0.118	-0.057	-0.012	0.020
						2	31	0.016	-0.035	-0.008	-0.015
						2	32	-0.007	0.008	-0.032	0.033
						2	33	-0.033	0.032	-0.028	-0.015
						2	34	-0.017	-0.010	-0.011	-0.015
						2	35	0.002	-0.019	0.041	0.002
						2	36	-0.000	0.000	-0.006	0.003
						2	37	0.001	-0.009	0.002	0.001
						2	38	-0.006	0.007	-0.005	-0.001
						2	39	-0.005	-0.022	-0.031	0.014

Table S4. The list of atomic coordinates of BP86/ZORA/def-TZVP(-f)/def2-SVP optimized geometry of the molecular fragment of **1**.

Ni	0.00190587860946	-0.11605254110058	2.62613171366988
Ni	1.57555364021958	-0.06702626224518	-0.04479291203122
Ni	-1.56696764016682	0.06317731164228	0.04785582651282
Ni	0.00598620258434	0.11257188143881	-2.62294853452867
C	3.32163395246037	2.19809057816675	-0.37081725170023
H	3.96465520604265	2.84121691151235	-0.99820873660409
C	2.71712602036261	-0.64816086642276	-2.50022237442526
C	3.99296977007183	-2.03485313435534	0.32700093362050
H	3.57130249830589	-2.67062586409402	-0.46542832275373
H	4.56485120173981	-2.66095912983098	1.03517440535449
H	4.65160483046233	-1.27822781127765	-0.13463754999668
O	2.86802896528876	-1.42633298301085	0.99550457951572
H	3.17884054092140	-0.78934603025615	1.66975726958800
C	-0.10996933247855	-2.40350200889226	0.94674773777588
C	0.20817349939176	-3.32234341739416	-0.06658253278337
H	0.64468621421731	-2.94255919806368	-0.99670757161578
C	-0.06834630749451	-4.68237208611525	0.13036886774129
H	0.15775019701224	-5.39972458766146	-0.66649888170430
C	-0.64915446088546	-5.12551474837679	1.33552682085747
H	-0.86169106562216	-6.19087881970934	1.48309408777165
C	-0.92957830439428	-4.21473893036132	2.36553501088438
H	-1.32599614060198	-4.57589049745628	3.32190939508864
C	-0.65260030949772	-2.84340493221280	2.18632692341693
C	-1.53665393068159	-1.96267220475903	4.23105881569666
H	-2.13785344315095	-2.88034033471805	4.36179944152814
C	-1.64087461324032	-0.98416915829383	5.27236357591368
C	-2.59684265674077	-1.22618815190782	6.29994354116329
H	-3.20447438414225	-2.13825671749143	6.22979298175394
C	-2.78895224595296	-0.34214248594022	7.35468980339157
H	-3.54040529073163	-0.54742947290126	8.12525206980282
C	-1.98816421499305	0.82654436356666	7.42244664996828
H	-2.12193564689090	1.53063784065349	8.25388505089827
C	-1.03499150025938	1.09497637054231	6.44596455224123
H	-0.41502899463086	1.99814849957625	6.48773279359159
C	-0.83538439803607	0.22593591720367	5.32616294757721
C	2.00655297749092	2.16381377623495	1.84151535348611
C	1.59128197406321	2.92262392894212	2.96712533125632
H	0.95690118702647	2.41590773826840	3.70470196016070
C	1.97189088526658	4.25529680116946	3.12058807119052
H	1.62554407523522	4.81351528021183	3.99975039103423
C	2.79179525146696	4.89113988898135	2.16033616827259
H	3.08384721132050	5.94033758471093	2.28040854406020
C	3.22030196109882	4.16109513118719	1.05658700147113
H	3.84543108680495	4.64035528138200	0.29200599915038
C	2.85366239326278	2.79926473337772	0.85430038404560
C	3.49855746385795	0.44336862429791	-2.00171211780241
C	4.66993062144021	0.83479361851631	-2.67965034448975
H	5.28244241904469	1.65488499429806	-2.28525293751984
C	5.07612525554428	0.14802538039424	-3.83422482101683
H	5.99141318036766	0.45349117055511	-4.35428796428402
C	4.32397171218947	-0.94434169300900	-4.30923169792944
H	4.64216047024561	-1.47863781280840	-5.21145416130889
C	3.15441164206586	-1.34212694243090	-3.64774812653111
H	2.54427618724918	-2.17427734403810	-4.01353327737538
N	-0.81013443285642	-1.82816413457278	3.14919169456366

N	3.00970682812379	1.00724806762662	-0.80964730682671
O	0.04505592324059	-1.06336129610593	0.79406512606003
O	0.04707923411350	0.57316336048436	4.42283905050778
O	1.59886938021679	0.89803703795446	1.73377774601273
O	1.57155430964882	-0.97701193914597	-1.86458236704224
C	-3.31352659057820	-2.20165558276440	0.37372568312523
H	-3.95711296753304	-2.84435919195548	1.00098075228847
C	-2.70930503804437	0.64512968401119	2.50258576618466
C	-3.98079459020475	2.03564210794273	-0.32302983042429
H	-3.55578677696604	2.67127556189463	0.46772375510184
H	-4.55235636181805	2.66239932784904	-1.03088211341984
H	-4.64051007295349	1.28129451439676	0.14078977823329
O	-2.85864789310884	1.42344229397897	-0.99287991892968
H	-3.17227257081212	0.78684815774281	-1.66613463485608
C	0.11835301255030	2.39980576193982	-0.94330572274088
C	-0.19934083434069	3.31851427077661	0.07031300696785
H	-0.63506442531884	2.93853305853146	1.00072638702838
C	0.07659975399586	4.67865300415621	-0.12668411097041
H	-0.14919927922787	5.39584712930507	0.67041090413293
C	0.65648030401718	5.12207774518978	-1.33218607080431
H	0.86857055964367	6.18751856352836	-1.47984195654619
C	0.93647599640880	4.21145268884348	-2.36244292780029
H	1.33203321237539	4.57281402413887	-3.31909474663344
C	0.65993060658042	2.84002755683775	-2.18323068244985
C	1.54320108220007	1.95978199053043	-4.22850334877643
H	2.14393473612982	2.87770320928910	-4.35953776923139
C	1.64714604795104	0.98142559062664	-5.26995668554549
C	2.60234005061298	1.22411089548516	-6.29810339738368
H	3.20949131881361	2.13651778976409	-6.22819448135914
C	2.79439985935986	0.34023196467062	-7.35300535706486
H	3.54535475128195	0.54595481207935	-8.12393322314136
C	1.99423508353463	-0.82889523074983	-7.42032682505139
H	2.12812303041904	-1.53295220498931	-8.25178366955336
C	1.04175180541252	-1.09796747528311	-6.44336155322712
H	0.42236238702312	-2.00155368620606	-6.48468759735687
C	0.84230565476290	-0.22916150963009	-5.32331176493718
C	-1.99766188793995	-2.16795840977595	-1.83805094226126
C	-1.58211412128921	-2.92691330460393	-2.96345737248513
H	-0.94756050778015	-2.42023586574268	-3.70090617630449
C	-1.96274301901554	-4.25957736034961	-3.11688946717735
H	-1.61620228918882	-4.81793161129308	-3.99588584658244
C	-2.78296984411269	-4.89524309106469	-2.15677548700244
H	-3.07502888042862	-5.94444417706548	-2.27681014345602
C	-3.21178987897478	-4.16504915298183	-1.05324635165572
H	-3.83724158016543	-4.64417099881667	-0.28884078868523
C	-2.84512080400472	-2.80323365999324	-0.85101533394020
C	-3.49081732860301	-0.44626624528720	2.00391619309544
C	-4.66263745727951	-0.83718088857466	2.68137807258647
H	-5.27517325868496	-1.65724672521201	2.28696466822587
C	-5.06920694727252	-0.15004563602707	3.83560530553070
H	-5.98468741204026	-0.45533337791745	4.35543345775810
C	-4.31703474033875	0.94229424670933	4.31068011331612
H	-4.63539432922635	1.47667447922015	5.21278941884989
C	-3.14693419505257	1.33943615682644	3.64976395752125
H	-2.53697560000381	2.17182677226733	4.01531109518860
N	0.81721101079086	1.82493879274673	-3.14629406057974
N	-3.00140199820634	-1.01082605457174	0.81242247029201

- -0.03635410749595 1.05964068799314 -0.79054622530390
- -0.03966343771006 -0.57672427183200 -4.41967315397311
- -1.58997314489401 -0.90223017500633 -1.73027772766914
- -1.56338624604010 0.97350721746652 1.86734141050829

Table S5. The list of atomic coordinates of BP86/ZORA/def-TZVP(-f)/def2-SVP optimized geometry of the molecular fragment of **2**.

Co	-0.11630024411217	0.06397717789635	2.66027716922900
Co	1.59497337404468	-0.12661735290340	-0.00991584947513
Co	-1.58858094833846	0.12320360421243	0.01209731547844
Co	0.12457424191310	-0.06705806773740	-2.65778878960423
C	3.33337310317440	2.15795506337089	-0.34835075187504
H	3.93856282481635	2.82735568689164	-0.98548404637528
C	2.80608368498450	-0.69386611902684	-2.48811863393338
C	4.00164068147349	-2.12554084711624	0.38446541690377
H	3.62537159355800	-2.72050666900396	-0.46073877327409
H	4.56768704029672	-2.78041544352505	1.07116869120243
H	4.65431330244371	-1.32400187807616	-0.00543543592395
O	2.83764082027605	-1.58710414453967	1.04602709883404
H	3.11198142482048	-1.00617910998977	1.78271179198968
C	-0.14233047305078	-2.38559728393014	0.99557156085814
C	0.13788196507300	-3.32775149959346	-0.01002408288268
H	0.53206465851266	-2.97392495307373	-0.96832885506311
C	-0.10692793267029	-4.68527497804748	0.23294137169367
H	0.08920591671246	-5.41783435623512	-0.55827037248013
C	-0.60796353815342	-5.10923952395730	1.48075513266067
H	-0.78826318757041	-6.17430697123230	1.66804947265528
C	-0.84264793197594	-4.17651887547438	2.50164441939934
H	-1.17039120078770	-4.51972030627708	3.49015904038472
C	-0.60556110004774	-2.80499778684655	2.26981123416899
C	-1.47631661369761	-1.90881475932299	4.29192864261427
H	-2.07643929013155	-2.83019664824248	4.39299118750418
C	-1.62325956880425	-0.95962066595434	5.35576954407370
C	-2.53410023906867	-1.28707957896033	6.40101636602840
H	-3.06977598013670	-2.24342272614045	6.33545973241332
C	-2.76274138750599	-0.43366262632585	7.47437100190283
H	-3.47316193388537	-0.70764129839286	8.26231248473943
C	-2.05647438253971	0.79364869789585	7.53815466273707
H	-2.22238493856235	1.47430112514596	8.38302055466822
C	-1.15744302799265	1.15069929795650	6.53694442640387
H	-0.61541787575744	2.10295838567033	6.56970780924909
C	-0.92524917760270	0.30926188860804	5.40769707205967
C	2.04917836801382	2.09756091283374	1.89188135854131
C	1.66070863095308	2.84913831693889	3.02958928861991
H	1.03889531866633	2.35109877176914	3.78295542235538
C	2.03954551950829	4.18336408525028	3.18591041728510
H	1.70757128622018	4.73332658106711	4.07542866630459
C	2.83890127200580	4.82405821491810	2.21430072529555
H	3.13284755176301	5.87301262862818	2.33258450656496
C	3.24756116872823	4.09809461926728	1.10054643305892
H	3.85907484244468	4.58152573637462	0.32780466197812
C	2.87877679967389	2.73721821733408	0.89290327569241
C	3.54033156152898	0.43006493866637	-1.99389442160431
C	4.66925226538433	0.89047240516340	-2.69987547113442
H	5.24918188694663	1.73686515557649	-2.31217643157619
C	5.07606046670002	0.24366860689689	-3.87746549806400
H	5.95689824272049	0.60570514049784	-4.42018501312635
C	4.36777272841203	-0.87841331393370	-4.34836494649222
H	4.68209368096175	-1.37889156441559	-5.27117713501043
C	3.24306386142250	-1.34945873261426	-3.65611225671534
H	2.66526337432987	-2.20600347997960	-4.01848301658058

N	-0.73288862802179	-1.76931408288181	3.21595604091350
N	3.04691012638191	0.95746557786766	-0.78556974042369
O	-0.01082579564382	-1.05293157987000	0.80132272174780
O	-0.11901438272586	0.73220993721990	4.46099852009905
O	1.61775480541982	0.82819964482591	1.77155779722198
O	1.68978663932574	-1.08331862694530	-1.82036154853142
C	-3.32639323095412	-2.16137060973291	0.35030155918833
H	-3.93166731146655	-2.83093074095684	0.98716398283073
C	-2.79838984307129	0.68982575045677	2.49085031241457
C	-3.99241582354924	2.12595734582454	-0.37890587143807
H	-3.61393472720288	2.71969481359037	0.46615958049850
H	-4.55772330613444	2.78240073639637	-1.06469953409792
H	-4.64637345124435	1.32563342321176	0.01133692419379
O	-2.83031598511339	1.58518330501691	-1.04204810212738
H	-3.10692143868570	1.00633945687024	-1.77946277165300
C	0.14947362984603	2.38241186379269	-0.99295221395292
C	-0.13120509941095	3.32445732096609	0.01259840475183
H	-0.52568576805744	2.97040561277942	0.97070464849343
C	0.11352553329476	4.68203788433779	-0.23016887240953
H	-0.08310185585287	5.41452161906264	0.56099036969695
C	0.61498770986894	5.10616380186008	-1.47773657261509
H	0.79514191376301	6.17127415779220	-1.66491929620405
C	0.85027720469152	4.17351974171463	-2.49858246752909
H	1.17834501536280	4.51677486185397	-3.48696875365218
C	0.61317388278031	2.80196726367859	-2.26696639880032
C	1.48498445351895	1.90596799233720	-4.28879912673247
H	2.08489947742949	2.82751950457231	-4.38968962026994
C	1.63255654317407	0.95689424783934	-5.35260441095839
C	2.54377996798193	1.28436837723888	-6.39750520717913
H	3.07933469693648	2.24076787193510	-6.33174592744688
C	2.77300741125267	0.43088873983395	-7.47063027576304
H	3.48385524783891	0.70485259783436	-8.25819637215490
C	2.06689196525844	-0.79650434596954	-7.53473880613540
H	2.23348019253082	-1.47730458867030	-8.37934875795803
C	1.16737444571365	-1.15355572292268	-6.53395952468559
H	0.62558441772952	-2.10593841055366	-6.56684701040111
C	0.93470294593634	-0.31207905378661	-5.40480309591991
C	-2.04156148321804	-2.10061174946725	-1.88973429397898
C	-1.65337135065904	-2.85187901193457	-3.02773463691237
H	-1.03118120349305	-2.35381598783161	-3.78077936731368
C	-2.03291586992703	-4.18583046769024	-3.18467131621151
H	-1.70116380629759	-4.73555440208525	-4.07442335041190
C	-2.83267822767912	-4.82656456315177	-2.21344836017131
H	-3.12713877867194	-5.87531506594519	-2.33224260791775
C	-3.24111997847711	-4.10087027820672	-1.09940345757766
H	-3.85301066759195	-4.58432909253394	-0.32698020330641
C	-2.87174555066986	-2.74024163906291	-0.89115279740370
C	-3.53292131601926	-0.43385626948616	1.99647811473164
C	-4.66161676318868	-0.89441752873421	2.70274150189347
H	-5.24168115777576	-1.74070336589741	2.31500239002118
C	-5.06797189475283	-0.24797807021477	3.88065807602825
H	-5.94857078557956	-0.61022194810269	4.42362982384929
C	-4.35951984158530	0.87398524855352	4.35162069554437
H	-4.67341605273444	1.37413257629233	5.27475968147347
C	-3.23497500710519	1.34515153003495	3.65918118719697
H	-2.65720579079861	2.20174234320962	4.02148102964675
N	0.74114550197060	1.76637803790567	-3.21314356742348

N	-3.03983773253684	-0.96099567452742	0.78788832233330
O	0.01782196291701	1.04972281679378	-0.79880061053213
O	0.12763749688997	-0.73489510868364	-4.45872731851043
O	-1.60930053662522	-0.83166711712460	-1.76876036228229
O	-1.68213712618907	1.07936294521541	1.82304859029576

Table S6. Energy levels (cm^{-1}) of ligand field multiplets in zero magnetic field derived from CASSCF/NEVPT2/ZORA/def2-TZVP(-f) calculations for optimized geometries of **1** and **2**.

	1 (Ni1)	**1** (Ni2)	**2** (Co1)	**2** (Co2)
0:	0.0000	0.0000	0.0000	0.0000
1:	21.3810	7.0626	0.0000	0.0000
2:	34.0850	11.6681	50.5862	173.4563
3:	4728.1611	8774.7291	50.5862	173.4563
4:	4830.0626	8893.6497	1980.5939	646.9658
5:	5019.9839	8985.4476	1980.5939	646.9658
6:	6013.2399	10124.6247	2087.8967	991.6236
7:	6061.8224	10156.1605	2087.8967	991.6236
8:	6194.1269	10246.5955	3694.5185	1189.1843
9:	10870.7909	13315.8535	3694.5185	1189.1843
10:	11211.6470	13476.6937	3818.5298	1359.9945
11:	11416.6945	13486.3411	3818.5298	1359.9945
12:	11935.9354	14479.4105	4983.1081	6627.2494
13:	12496.3035	16379.6097	4983.1081	6627.2494
14:	12628.6394	17067.9627	5124.1003	8120.0568
15:	12949.7427	17122.6894	5124.1003	8120.0568
16:	15201.8863	17174.7629	7549.7026	8181.5547
17:	15324.9878	18994.6675	7549.7026	8181.5547
18:	15502.9715	19189.3710	7621.2264	10892.4309
19:	15862.5169	19254.6935	7621.2264	10892.4309
20:	16256.5449	19961.7512	11283.4988	10959.6303
21:	16343.2054	20005.2862	11283.4988	10959.6303
22:	16820.3780	20141.2694	11338.4882	11751.3199
23:	20439.7012	24637.9504	11338.4882	11751.3199
24:	21096.8308	25534.3083	11538.7943	12332.4446
25:	24063.3638	28603.4214	11538.7943	12332.4446
26:	24184.1812	29115.6156	14349.3723	12425.6884
27:	24201.1658	29239.4813	14349.3723	12425.6884
28:	25651.7587	29320.0196	14483.7641	15416.8511
29:	26966.5683	29840.8778	14483.7641	15416.8511
30:	27917.0099	30645.1897	14613.6528	16843.1659
31:	28006.5000	31371.3015	14613.6528	16843.1659
32:	28264.8757	31556.1886	17423.4126	18457.2550
33:	29242.6119	31671.5027	17423.4126	18457.2550
34:	29338.4247	31934.5506	18118.7352	18969.3854
35:	29457.5088	32026.7306	18118.7352	18969.3854
36:	30305.4200	32079.2287	19092.9205	19671.2668
37:	32394.3853	34808.1826	19092.9205	19671.2668
38:	33887.4956	35403.1718	19293.2839	21215.3309
39:	35443.3389	40703.1789	19293.2839	21215.3309
40:	36150.7967	41225.6923	19349.3740	21819.7530
41:	36931.2812	41629.7181	19349.3740	21819.7530
42:	37686.6067	42242.0670	19881.8275	21991.8584
43:	38106.9950	42623.0358	19881.8275	21991.8584
44:	62878.6029	67157.3723	20584.2900	22111.3478
45:			20584.2900	22111.3478
46:			20917.3870	22384.6983
47:			20917.3870	22384.6983
48:			22029.6689	22947.6227
49:			22029.6689	22947.6227
50:			22414.7789	23163.8929
51:			22414.7789	23163.8929
52:			22624.6513	23325.7693

53:			22624.6513	23325.7694
54:			22748.1535	23893.8713
55:			22748.1535	23893.8713
56:			23404.9877	24147.6368
57:			23404.9877	24147.6368
58:			24004.1645	25437.3391
59:			24004.1645	25437.3391
60:			24974.2862	26929.0313
61:			24974.2862	26929.0313
62:			25075.4738	26999.7031
63:			25075.4739	26999.7031
64:			26854.0549	29073.5019
65:			26854.0549	29073.5019
66:			27013.1134	29305.3574
67:			27013.1134	29305.3574
68:			28524.1043	29693.7320
69:			28524.1043	29693.7320
70:			29173.7402	30628.0554
71:			29173.7402	30628.0554
72:			29680.4309	32085.0758
73:			29680.4309	32085.0758
74:			30515.3214	32634.9222
75:			30515.3214	32634.9222
76:			31082.0525	33062.5394
77:			31082.0525	33062.5394
78:			31367.3296	34233.5178
79:			31367.3296	34233.5178
80:			31649.0077	35898.2176
81:			31649.0077	35898.2176
82:			31893.5547	36040.4073
83:			31893.5547	36040.4073
84:			32658.5186	36431.7324
85:			32658.5186	36431.7324
86:			33247.3863	38044.4541
87:			33247.3863	38044.4541
88:			33760.0150	39107.0070
89:			33760.0150	39107.0070
90:			35066.5118	39343.7438
91:			35066.5118	39343.7438
92:			35520.7961	39912.1843
93:			35520.7961	39912.1843
94:			36051.2024	40371.6928
95:			36051.2024	40371.6928
96:			41459.7427	42544.1856
97:			41459.7427	42544.1856
98:			42249.7782	44377.7584
99:			42249.7782	44377.7584
100:			42493.7965	45159.3965
101:			42493.7965	45159.3965
102:			44349.8044	46274.8552
103:			44349.8044	46274.8552
104:			44589.9833	47116.4854
105:			44589.9833	47116.4855
106:			45048.4708	47524.2571
107:			45048.4708	47524.2571
108:			45190.7928	47664.5454
109:			45190.7928	47664.5454

110:			61522.8344	64839.7765
111:			61522.8344	64839.7765
112:			62193.1914	66645.0790
113:			62193.1914	66645.0790
114:			64416.0524	67707.1085
115:			64416.0524	67707.1085
116:			66053.3646	68450.1743
117:			66053.3646	68450.1743
118:			66712.7501	69052.7150
119:			66712.7501	69052.7150

Table S7. Individual contributions to *D*-tensor for optimized geometries of **1** and **2** calculated by CASSCF/NEVPT2/ZORA/def2-TZVP(-f).

		1 (Ni1)		**1** (Ni2)				**2** (Co1)		**2** (Co2)	
(2*S*+1)	Root	*D*	*E*	*D*	*E*	(2*S*+1)	Root	*D*	*E*	*D*	*E*
3	0	0.000	0.000	0.000	-0.000	4	0	0.000	0.000	0.000	0.000
3	1	37.694	38.277	22.608	21.449	4	1	-44.922	-0.037	42.538	41.920
3	2	30.471	-30.841	18.537	-17.969	4	2	8.307	-8.338	21.202	-19.032
3	3	-17.822	0.974	-28.755	-0.335	4	3	5.190	-5.366	-9.518	1.500
3	4	-12.586	-0.325	-0.167	-0.027	4	4	6.847	6.857	3.482	-3.592
3	5	0.948	-0.901	0.220	-0.121	4	5	0.686	-0.536	0.799	-0.819
3	6	-0.229	0.191	0.140	-0.026	4	6	0.268	0.286	0.023	0.025
3	7	-0.033	-0.002	-0.004	-0.006	4	7	0.001	-0.000	0.131	-0.135
3	8	0.108	-0.109	0.025	-0.025	4	8	0.032	0.048	0.062	-0.060
3	9	0.049	0.048	0.017	0.014	4	9	0.048	-0.044	0.092	0.092
1	0	-0.289	0.136	-0.019	-0.018	2	0	0.814	-0.682	3.525	0.253
1	1	-0.040	0.006	-0.003	-0.001	2	1	-0.296	0.223	-0.753	-2.893
1	2	-7.908	-7.956	-7.322	-7.288	2	2	0.740	-0.075	-0.124	0.124
1	3	-7.421	7.418	-6.430	6.539	2	3	1.978	-0.029	-0.423	0.421
1	4	8.797	-0.066	11.301	0.068	2	4	-0.077	0.076	-1.221	-1.220
1	5	2.672	-0.049	0.238	0.004	2	5	0.261	0.008	-0.105	0.059
1	6	-0.028	0.007	0.025	-0.004	2	6	1.854	-0.154	-0.804	0.802
1	7	0.051	0.124	-0.143	0.143	2	7	-1.616	1.710	0.214	-0.049
1	8	0.334	0.006	-0.069	-0.026	2	8	0.045	-1.170	-0.003	-0.000
1	9	-0.198	0.006	-0.134	-0.096	2	9	-0.169	-0.151	1.064	0.001
1	10	-0.153	-0.186	-0.014	0.047	2	10	-0.142	0.141	2.694	-0.003
1	11	-0.471	-0.049	0.094	0.370	2	11	0.000	0.000	-0.040	-0.040
1	12	-0.429	0.301	-0.303	-0.360	2	12	-0.050	0.043	-0.176	-0.182
1	13	1.560	0.140	0.772	0.149	2	13	0.325	0.002	-0.223	0.203
1	14	-0.002	0.002	-0.001	-0.001	2	14	-0.191	0.182	0.024	0.100
						2	15	0.016	0.071	-0.002	0.005
						2	16	-0.157	0.159	0.032	-0.003
						2	17	-0.069	-0.017	-0.088	-0.086
						2	18	0.006	-0.010	-0.410	-0.675
						2	19	0.078	0.056	0.150	0.028
						2	20	-0.629	-0.485	-0.317	0.347
						2	21	-0.584	-0.473	-0.005	-0.009
						2	22	0.056	0.039	0.213	0.051
						2	23	0.393	0.008	-0.323	0.381
						2	24	-0.164	0.170	0.044	0.000
						2	25	0.007	-0.085	-0.019	0.037
						2	26	-0.003	0.002	0.129	-0.003
						2	27	-0.003	-0.007	-0.133	-0.110
						2	28	-0.144	0.126	0.242	-0.046
						2	29	-0.004	0.005	-0.134	0.152
						2	30	0.008	-0.088	-0.007	0.007
						2	31	0.061	-0.016	-0.004	-0.003
						2	32	-0.007	0.005	-0.009	0.009
						2	33	-0.008	0.020	-0.027	-0.027
						2	34	0.002	0.000	-0.042	-0.046
						2	35	0.032	-0.001	-0.010	-0.045
						2	36	-0.000	0.000	0.003	0.000
						2	37	0.004	-0.003	-0.002	-0.002
						2	38	-0.013	-0.002	0.001	0.001
						2	39	0.018	-0.001	0.040	0.005