Supplementary Information

Counter-complementarity control of weak exchange interaction in bent {Ni(II)$_3$} complex with μ-phenoxide-μ-carboxylate double bridge

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Table S1. Ni(II) coordination spheres bond lengths [Å] and angles [deg] in complex **1**.

Ni(1)-O(6)’	2.013(4)
Ni(1)-O(6)	2.013(4)
Ni(1)-O(2)’	2.029(4)
Ni(1)-O(2)	2.029(4)
Ni(1)-O(1)’	2.111(4)
Ni(1)-O(1)	2.111(4)
Ni(2)-N(1)	2.030(4)
Ni(2)-O(7)’	2.046(4)
Ni(2)-O(3)	2.049(4)
Ni(2)-O(2)	2.051(4)
Ni(2)-O(4)	2.091(4)
Ni(2)-O(5)	2.125(5)
O(6)’-Ni(1)-O(6)	90.2(3)
O(6)’-Ni(1)-O(2)’	88.56(17)
O(6)-Ni(1)-O(2)’	101.39(16)
O(6)’-Ni(1)-O(2)	101.39(16)
O(6)-Ni(1)-O(2)	88.57(17)
O(2)’-Ni(1)-O(2)	166.0(2)
O(6)’-Ni(1)-O(1)’	177.3(2)
O(6)-Ni(1)-O(1)’	92.42(19)
O(2)’-Ni(1)-O(1)’	91.56(16)
O(2)-Ni(1)-O(1)’	78.03(16)
O(6)’-Ni(1)-O(1)	92.42(19)
O(6)-Ni(1)-O(1)	177.3(2)
O(2)’-Ni(1)-O(1)	78.03(15)
O(2)-Ni(1)-O(1)	91.56(16)
O(1)’-Ni(1)-O(1)	85.0(3)
N(1)-Ni(2)-O(7)’	169.7(2)
N(1)-Ni(2)-O(3)	82.35(18)
O(7)’-Ni(2)-O(3)	88.73(16)
N(1)-Ni(2)-O(2)	89.81(18)
O(7)’-Ni(2)-O(2)	99.51(16)
O(3)-Ni(2)-O(2)	170.65(16)
N(1)-Ni(2)-O(4)	91.88(18)
O(7)’-Ni(2)-O(4)	93.35(16)
O(3)-Ni(2)-O(4)	90.69(17)
O(2)-Ni(2)-O(4)	84.47(17)
N(1)-Ni(2)-O(5)	90.64(18)
O(7)’-Ni(2)-O(5)	84.43(16)
O(3)-Ni(2)-O(5)	91.3(2)
O(2)-Ni(2)-O(5)	93.85(19)
O(4)-Ni(2)-O(5)	176.97(15)

Symm.Op.: ‘ -x,y,-z+3/2

Table S2. Hydrogen bonds metric in complex **1** structure [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(1O4)...O(9)	0.898(10)	1.900(10)	2.707(7)	149(3)
O(4)-H(2O4)...O(6)	0.907(10)	1.922(14)	2.816(6)	168(6)
O(5)-H(2O5)...O(3)	0.90(2)	1.98(4)	2.840(6)	159(8)
O(8)-H(1O8)...O(3)'	0.90(2)	1.72(4)	2.581(7)	161(10)

Symm. Op.: ' -x,-y,-z+1

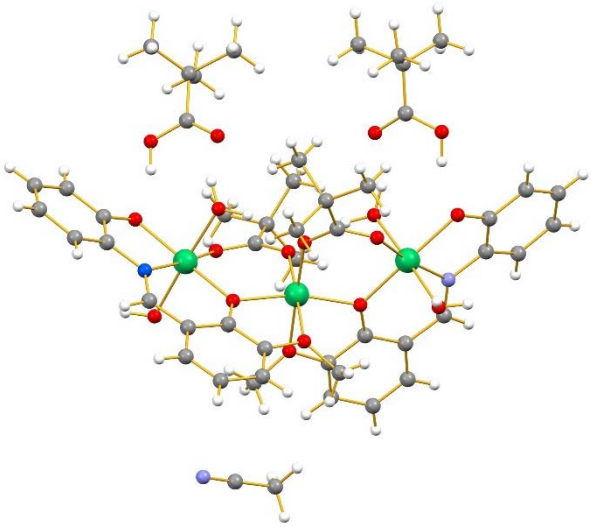

Figure SI1. Ball and stick molecular representation of complex **1** and solvent molecules content in crystal structure. Colour code: Green: Ni; Red: O; Blue: N; Grey: C; White: H.

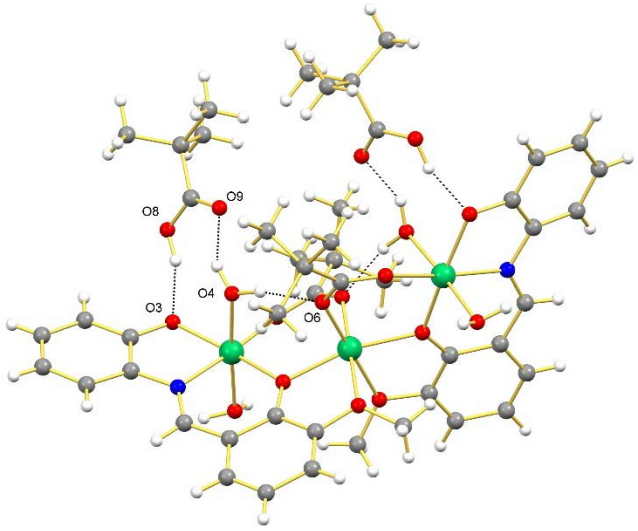

Figure SI2. Ball and stick molecular representation of complex **1** showing the intra-molecular H-interactions pattern. Colour code: Green: Ni; Red: O; Blue: N; Grey: C; White: H.

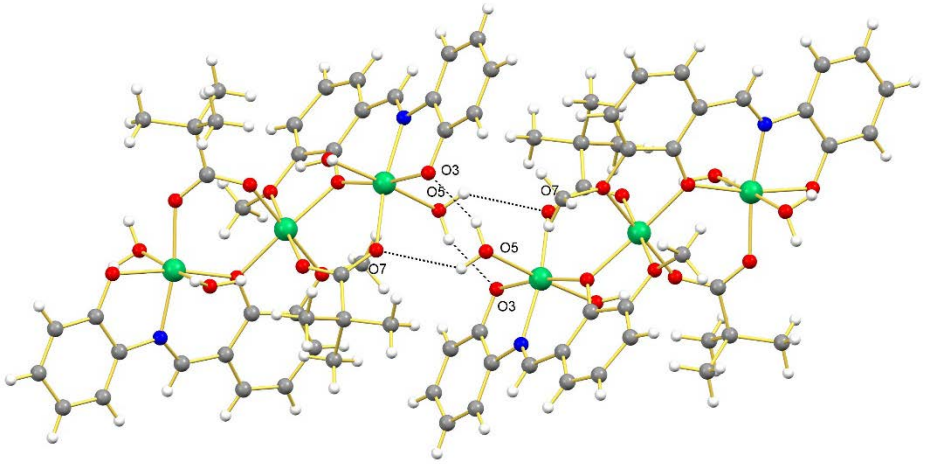

Figure SI3. Ball and stick molecular representation of complex **1** showing the inter-molecular H-interactions pattern. Colour code: Green: Ni; Red: O; Blue: N; Grey: C; White: H.

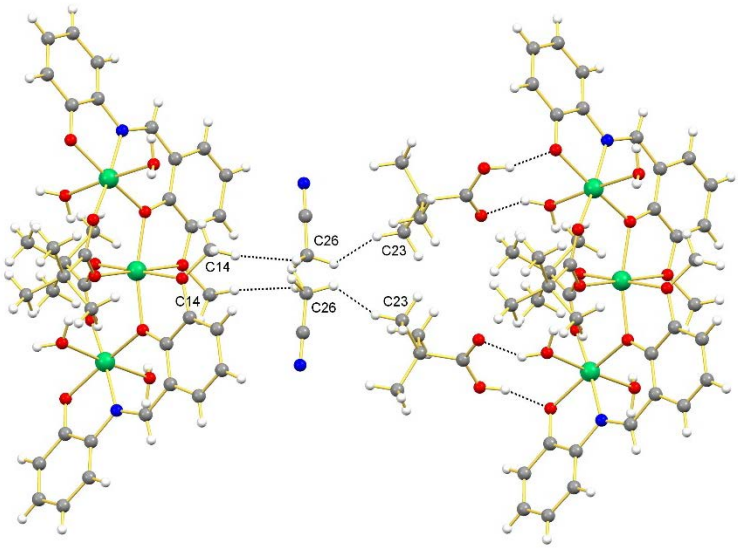

Figure SI4. Ball and stick molecular representation of complex **1** showing the short contact interactions between acetonitrile solvent molecules and alkyl groups of surrounding complex molecules. Both disordered components of acetonitrile are shown (each with 0.5 occupancy factor). Colour code: Green: Ni; Red: O; Blue: N; Grey: C; White: H.

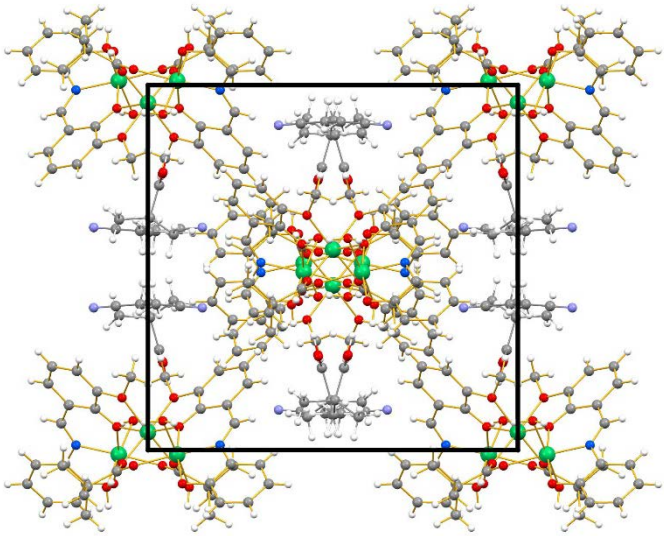

Figure SI5. Crystal structure packing. View along *c* direction showing complex **1** molecules alignment as well as acetonitrile molecules void filling role. Colour code: Green: Ni; Red: O; Blue: N; Grey: C; White: H.

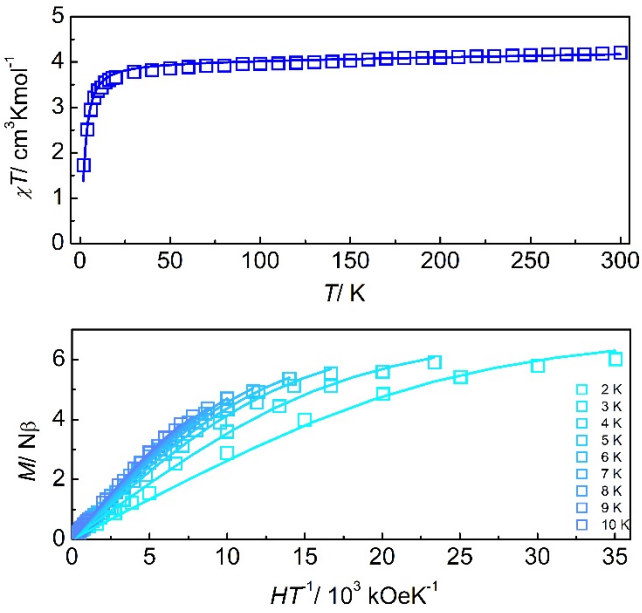

Figure SI6. Top: χT vs. T data of complex **1** under a 1000 Oe magnetic field. Bottom: reduced magnetization data of complex **1** in the range 2-10 K under magnetic fields up to 70 kOe. Open symbols: experimental data; full lines: simulation employing best fitting parameters with a positive D value as described in the text.

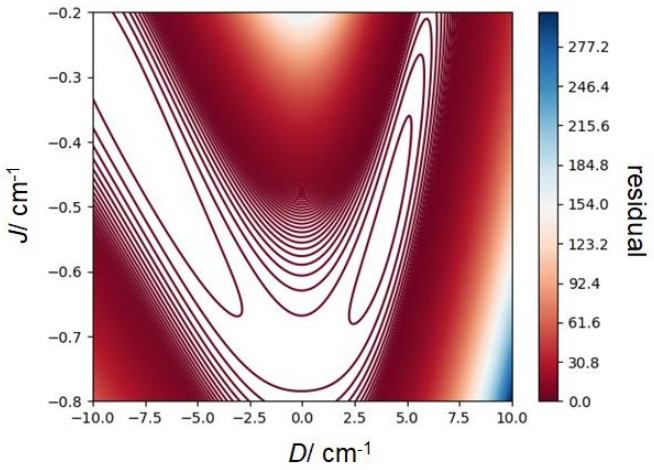

Figure SI7. Residual contour plot of simultaneous magnetization and susceptibility magnetic data simulation according to spin Hamiltonian of Eq. 1 with g = 2.31.

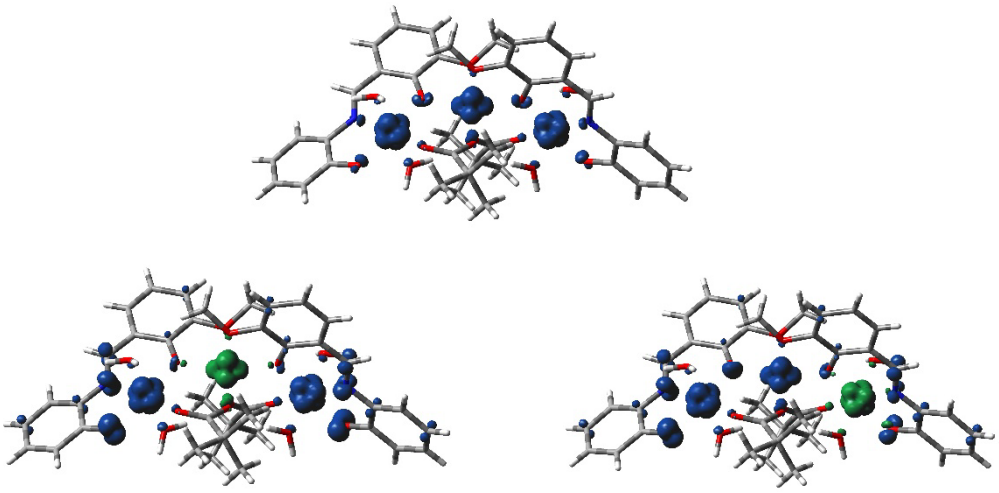

Figure SI8. Spin density iso-surfaces (0.02 a.u.), as arising from BS calculations of complex **1** (see details in text). Top: HS state; Bottom: BS states converged after flipping central (left) and terminal (right) Ni(II) spin densities.

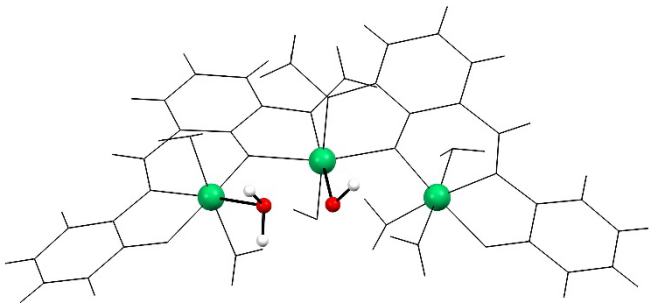

Figure SI9. Molecular model of complex **1**, with the replacement of the μ_2-carboxylate ligands by an aqua and hydroxo ligands; employed for BS calculations (see text).

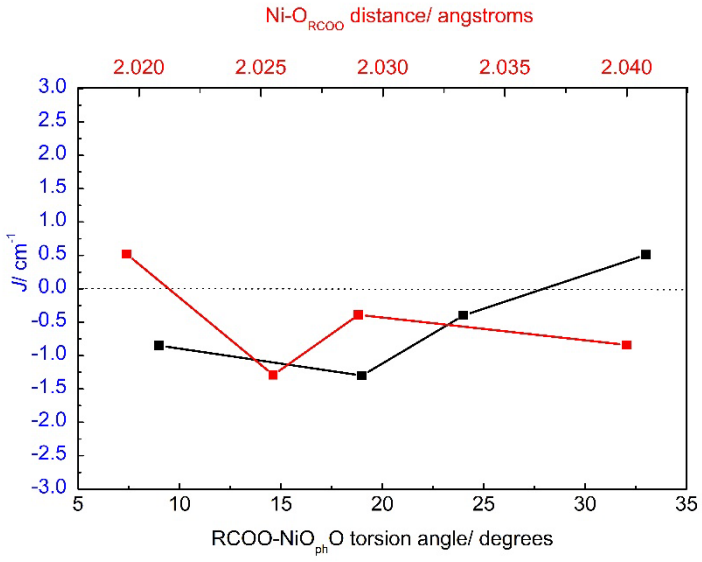

Figure SI10. Magneto-structural correlation of the exchange interaction parameter *J* with metric values related to the carboxylate bridge responsible of the counter-complementarity effect.