Electronic Supplementary Information for CrystEngComm

Supramolecular patterns of cationic and neutral Ni(II) complexes from the interplay of hydrogen-bonding, stacking interactions and metal-coordination motifs

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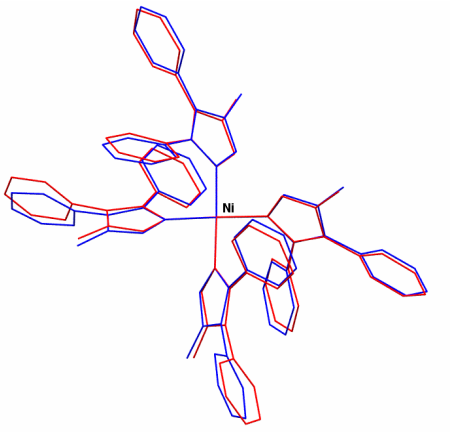
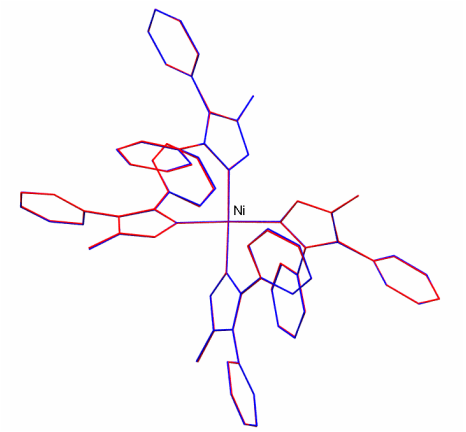
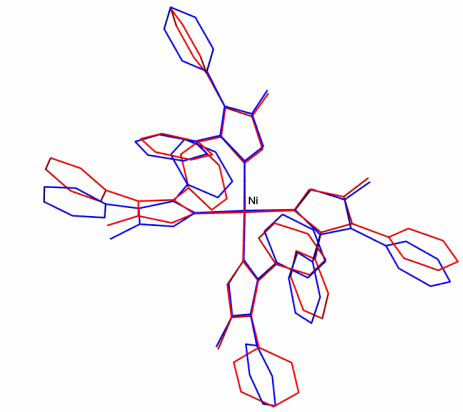


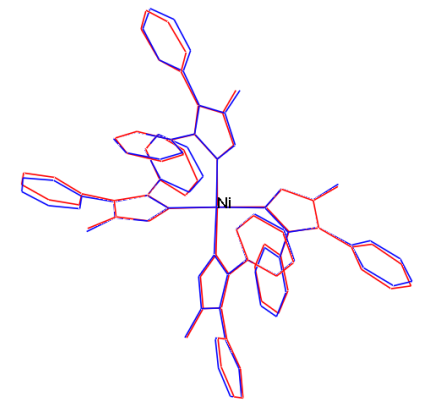
1–**2**: r.m.s. deviation = 0.360 Å



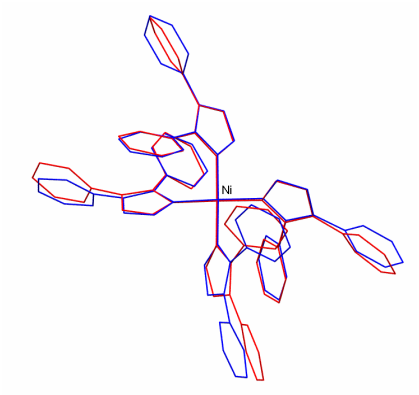
1–**3**: r.m.s. deviation = 0.039 Å



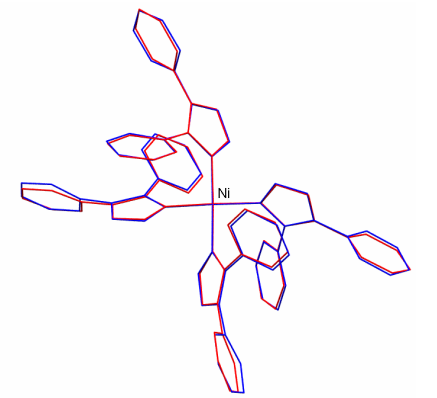
1–**4**: r.m.s. deviation = 0.466 Å



1–**5**: r.m.s. deviation = 0.152 Å



1–**6**: r.m.s. deviation = 0.524 Å



1–**9**: r.m.s. deviation = 0.124 Å

Figure S1. Representative molecular overlays of the $[NiL_4]^{2+}$ and $[Ni(HL')_4]^{2+}$ cations found in compounds **1**–**5** and **6**–**10**, respectively. The cation of **1** has been taken as the reference molecule. The fit was performed over all pairs of equivalent atoms. The conformation of the cations is similar; the largest deviations occur for the phenyl rings not involved in intramolecular $\pi\cdots\pi$ stackings. The methyl group of the $[NiL_4]^{2+}$ in the overlays between $[NiL_4]^{2+}$ and $[Ni(HL')_4]^{2+}$ has been removed for the shake of comparison. The r.m.s. deviation for the pairs not shown here is: 0.616 Å (**1**–**7**), 0.141 Å (**1**–**8**), and 0.200 Å (**1**–**10**). The cation of compound **1** is in blue; those of **2**, **3**, **4**, **5**, **6** and **9** are in red.

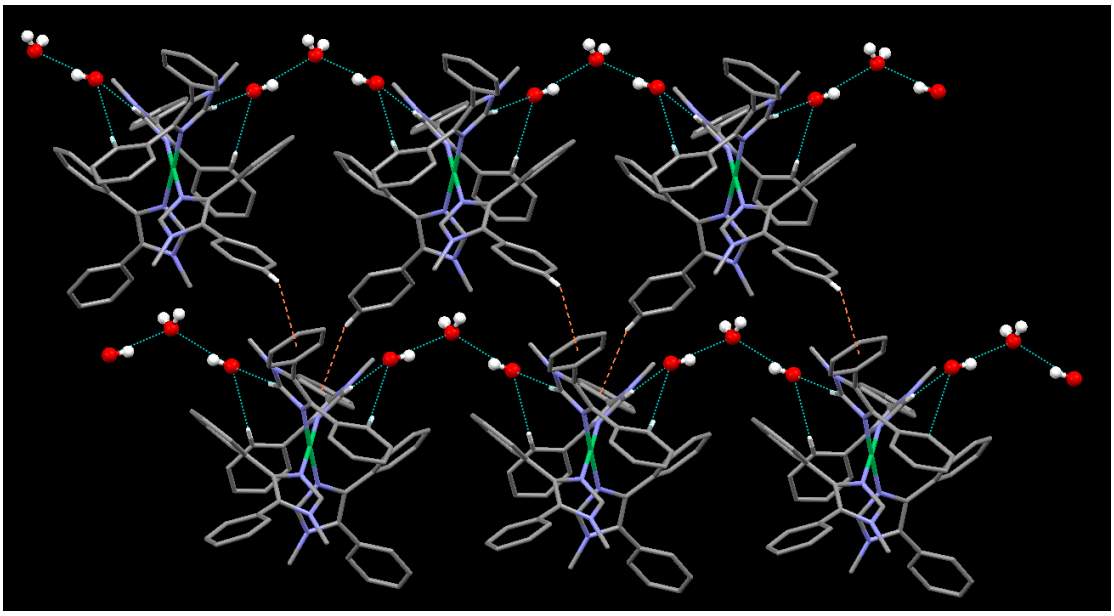
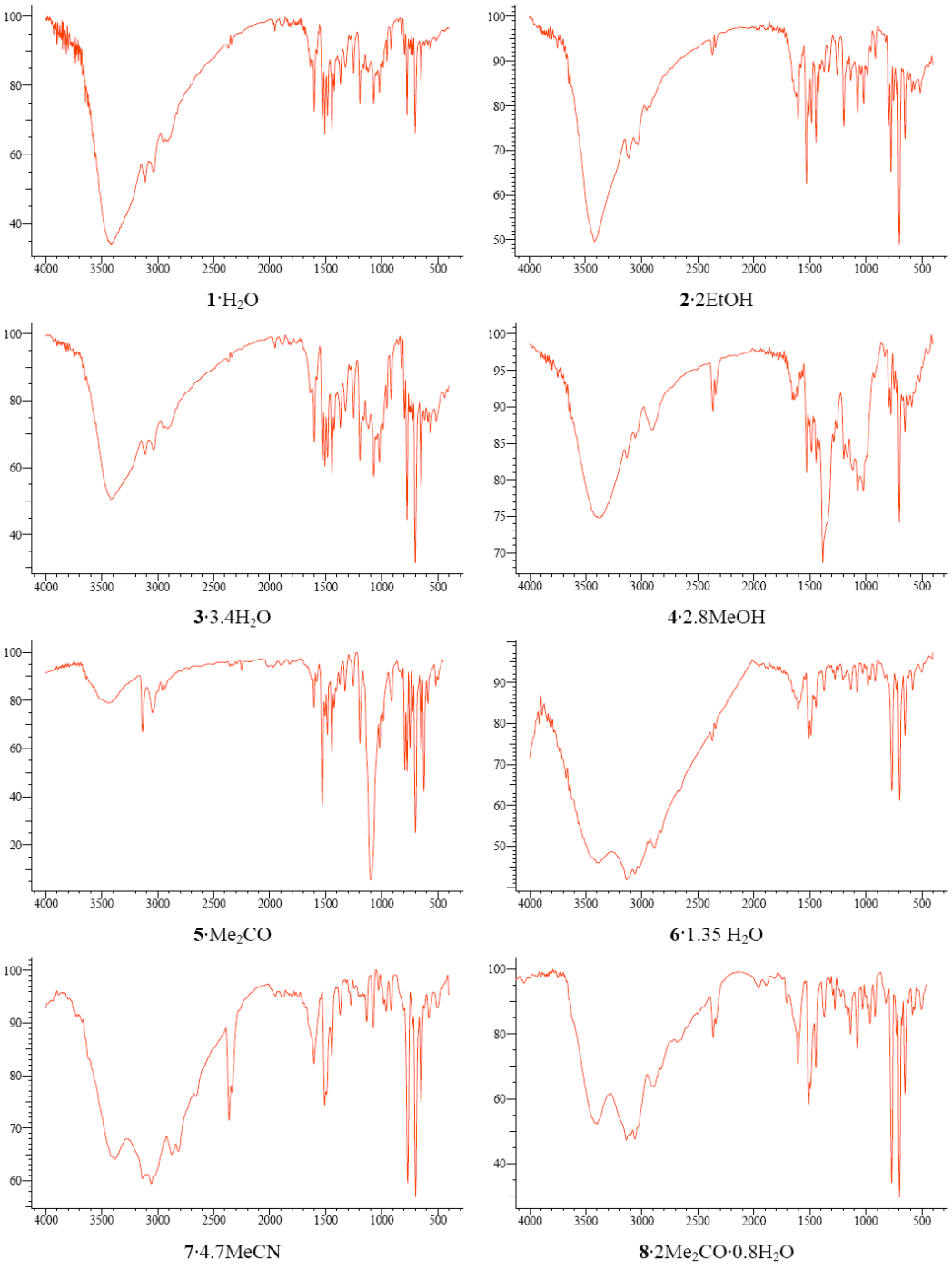


Figure S2. The H-bonded 2D structure of compound $[NiL_4](OH)_2 \cdot H_2O$ (**1**). The OH^- /H_2O components of the counterion/solvent cluster are held together *via* strong O–H···O bonds (cyan dotted lines). The supramolecular assembly is organized around the $[NiL_4]^{2+}$ cations *via* weak C–H···O interactions with the surrounding clusters (cyan dotted lines). The structure is further stabilized *via* weak C–H···π interactions between the $[NiL_4]^{2+}$ cations (orange dashed lines).



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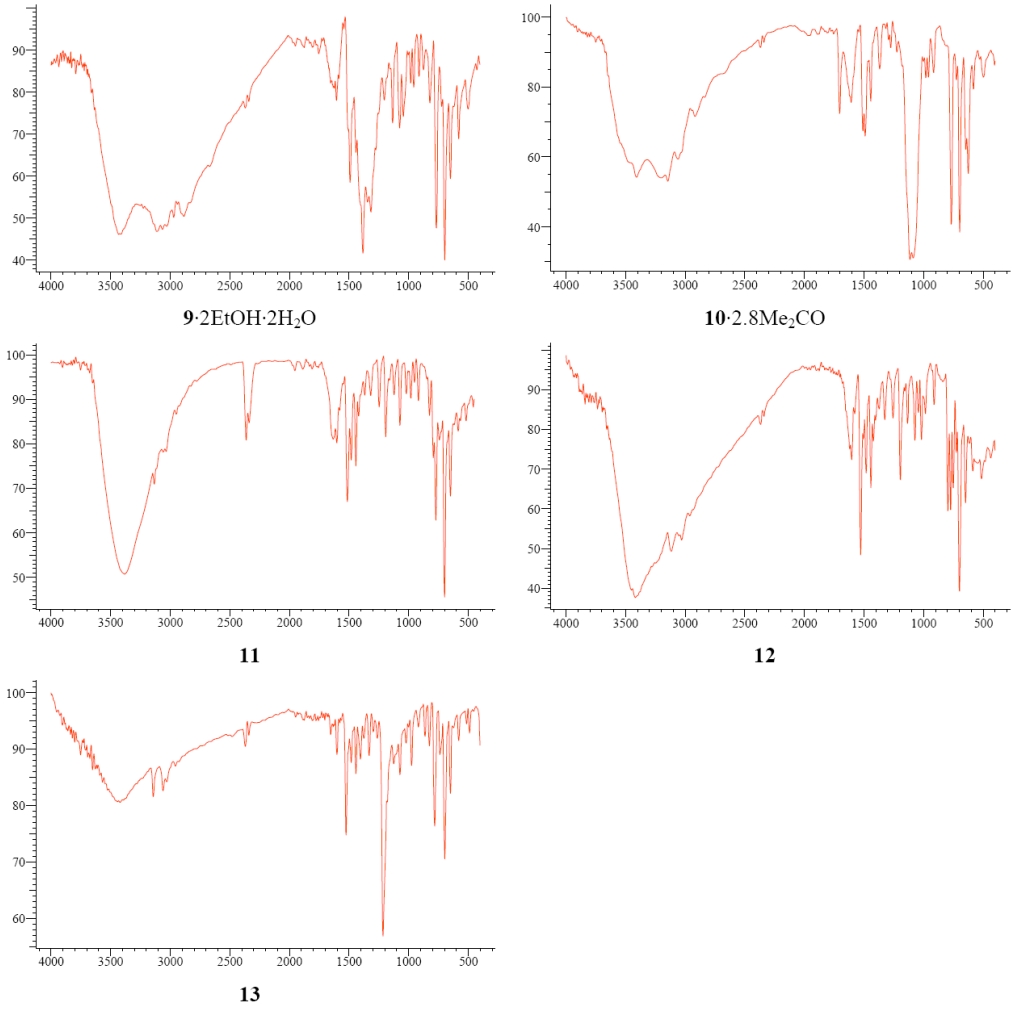

Figure S3. The IR spectra of the studied compounds **1**–**13**.
X-axis: Wavenumbers (cm^{-1}); Y-axis: % Transmittance.

Table S1. Geometry (Å, º) of the strong hydrogen-bonding motifs in compounds **6**–**10**.

D–H· · ·A	D–H	H· · ·A	D· · ·A	<(DHA)	Symmetry operation of A
6					
N1A–H1A···Cl5	0.86(2)	2.34(2)	3.134(3)	154(2)	x, –1+y, z
N1B–H1B···Cl6A	0.83(3)	2.28(3)	3.064(3)	157(3)	x, y, 1+z
N1C–H1C···Cl5	0.86(2)	2.28(2)	3.133(3)	170(2)	1–x, 1–y, 1–z
N1D–H1D···O1A	0.87(2)	1.87(2)	2.719(5)	165(3)	2–x, 1–y, 1–z
N1E–H1E···Cl6A	0.86(3)	2.15(3)	3.002(3)	173(3)	x, y, z
N1F–H1F···Cl4	0.87(3)	2.33(3)	3.154(3)	159(2)	2–x, 1–y, 1–z
N1G–H1G···Cl1	0.85(3)	2.41(3)	3.190(3)	154(3)	1–x, –y, 1–z
N1H–H1H···Cl5	0.88(3)	2.24(3)	3.075(3)	159(3)	2–x, 1–y, 1–z
7					
N1A–H1A···Br1	0.84(2)	2.41(2)	3.250(3)	173(2)	–x, 1–y, 1–z
N1C–H1C···Br1	0.83(3)	2.48(2)	3.269(2)	160(2)	1–x, 1–y, 1–z
8					
N1A–H1A···I1A	0.87(4)	2.68(4)	3.509(4)	160(4)	1–x, 1–y, z
N1B–H1B···I1A	0.86(4)	2.62(4)	3.477(4)	177(5)	x, 1/2+y, –1/2+z
9					
N1A–H1A···O1	0.86(3)	1.94(3)	2.787(3)	169(3)	x, 2–y, 1/2+z
N1B–H1B···O2	0.88(3)	1.96(3)	2.835(3)	175(2)	x, y, z
10					
N1A–H1A···O8	0.89(6)	1.97(6)	2.861(7)	174(8)	1+x, y, z
N1B–H1B···O1	0.89(3)	2.00(3)	2.868(8)	168(6)	1+x, y, 1+z
N1C–H1C···O2	0.88(4)	1.97(4)	2.840(7)	168(4)	x, y, z
N1D–H1D···O5	0.87(5)	1.98(5)	2.851(7)	172(5)	x, y, z