Electronic Supplementary Information

The curious cases of tetrahydrosalen-type ligands interacting with Ni(II): structures and ligand-based oxidation reactions

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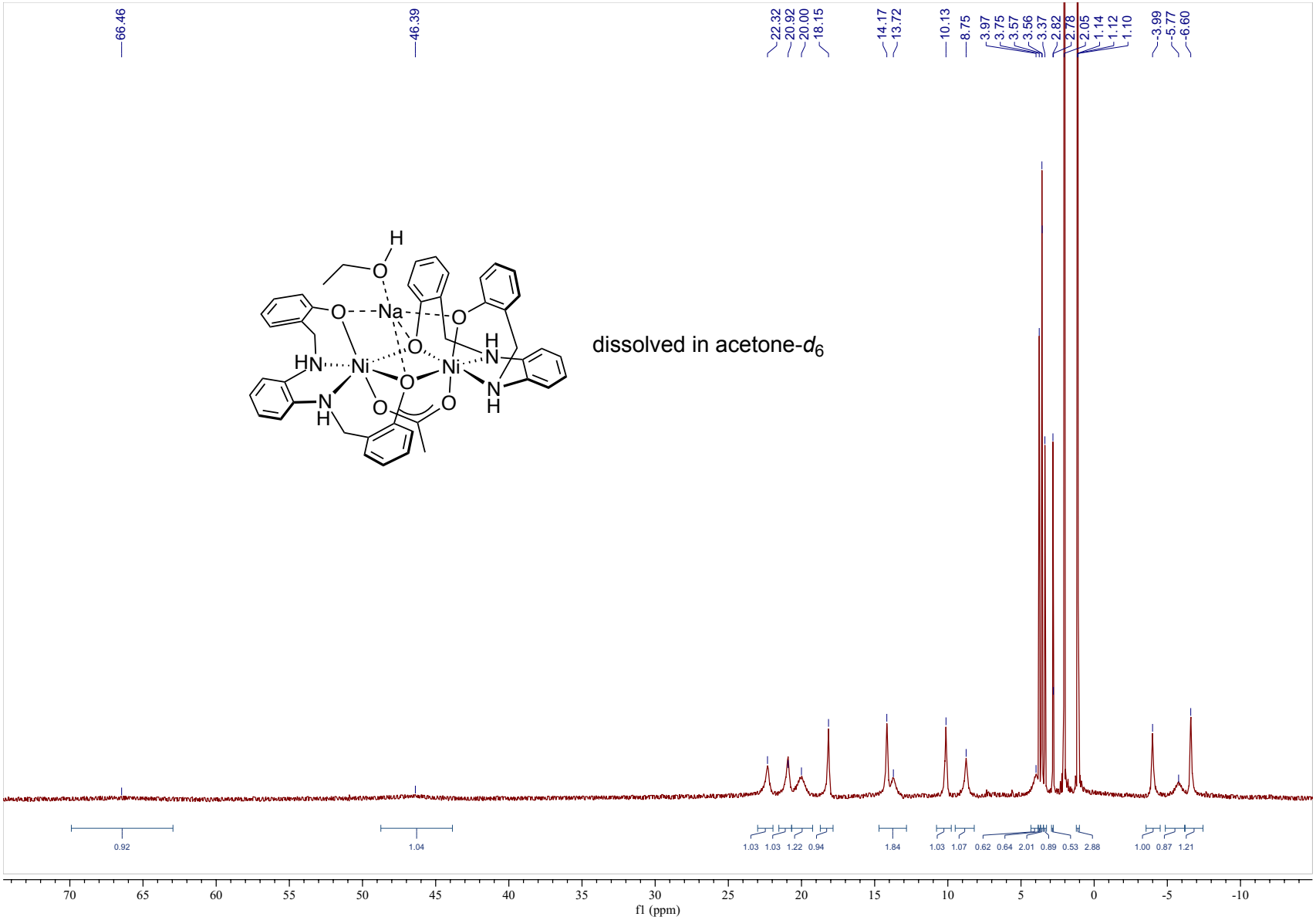


Fig. S1 ^{1}H NMR (400 MHz, acetone-d_6, 23 °C) spectrum of Na[Ni_2(salophan)$_2$(OAc)]

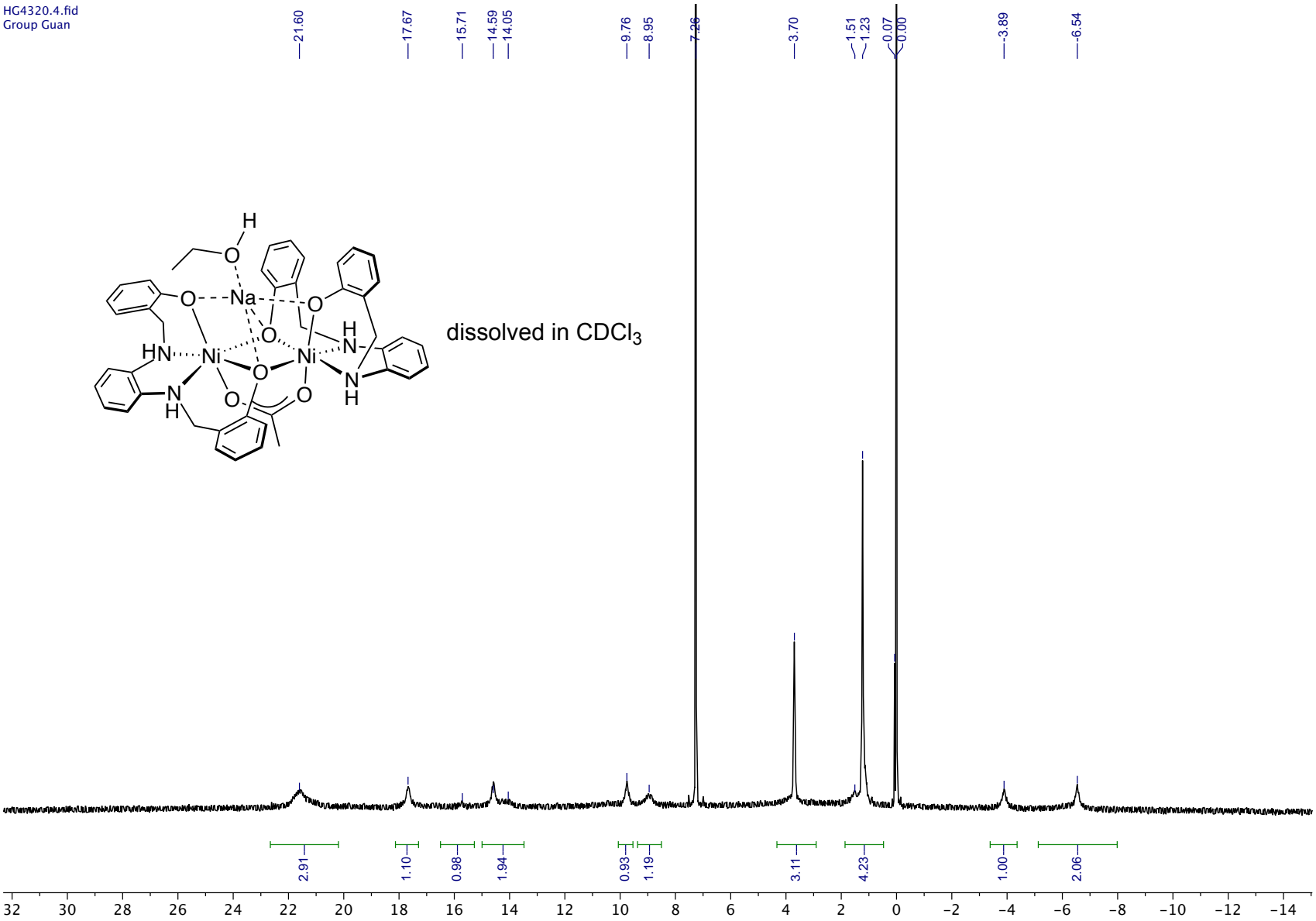


Fig. S2 ^{1}H NMR (400 MHz, $CDCl_3$, with TMS, 23 °C) spectrum of $Na[Ni_2(salophan)_2(OAc)]$

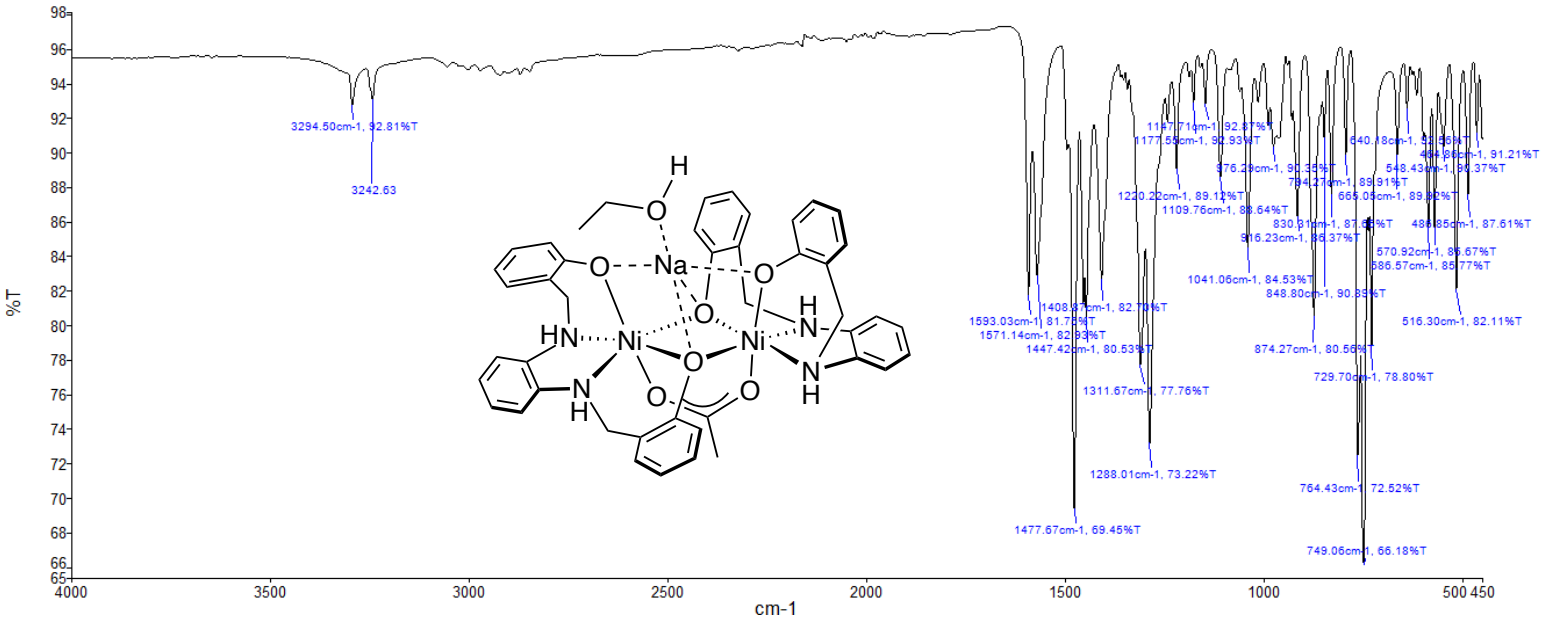


Fig. S3 IR spectrum of $Na[Ni_2(salophan)_2(OAc)]$•EtOH (solid sample)

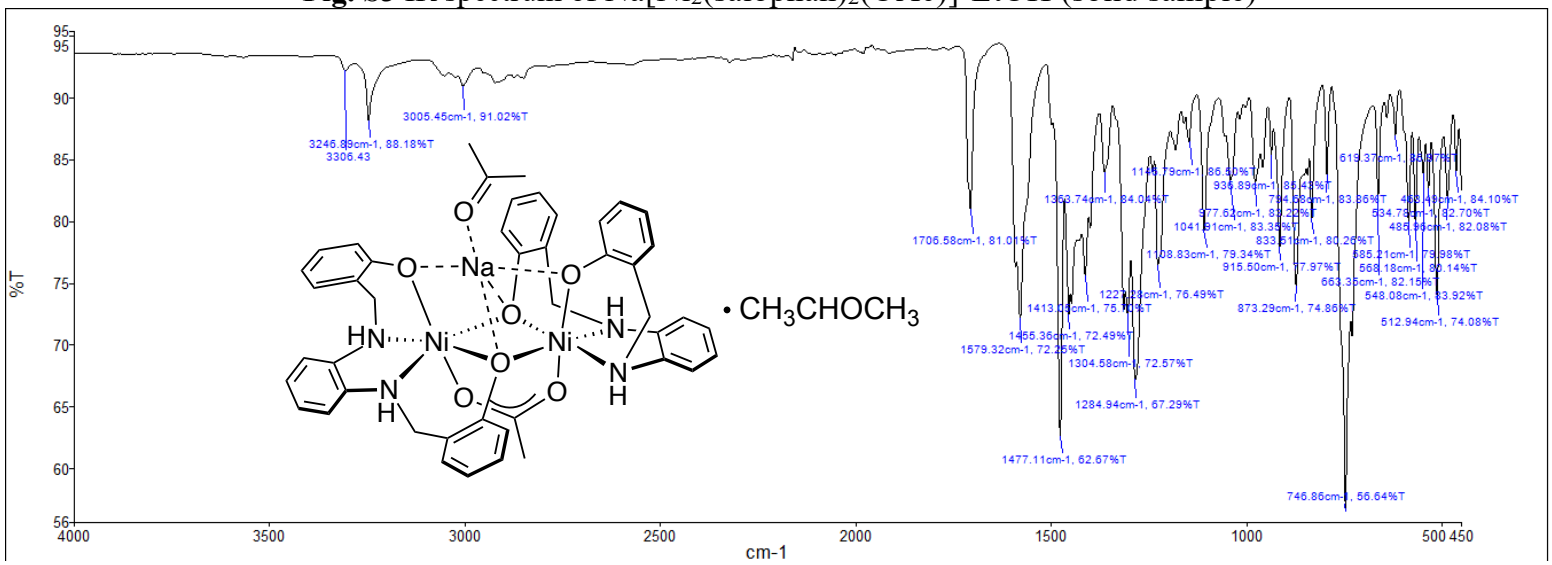


Fig. S4 IR spectrum of $Na[Ni_2(salophan)_2(OAc)]$•$2CH_3COCH_3$ (solid sample)

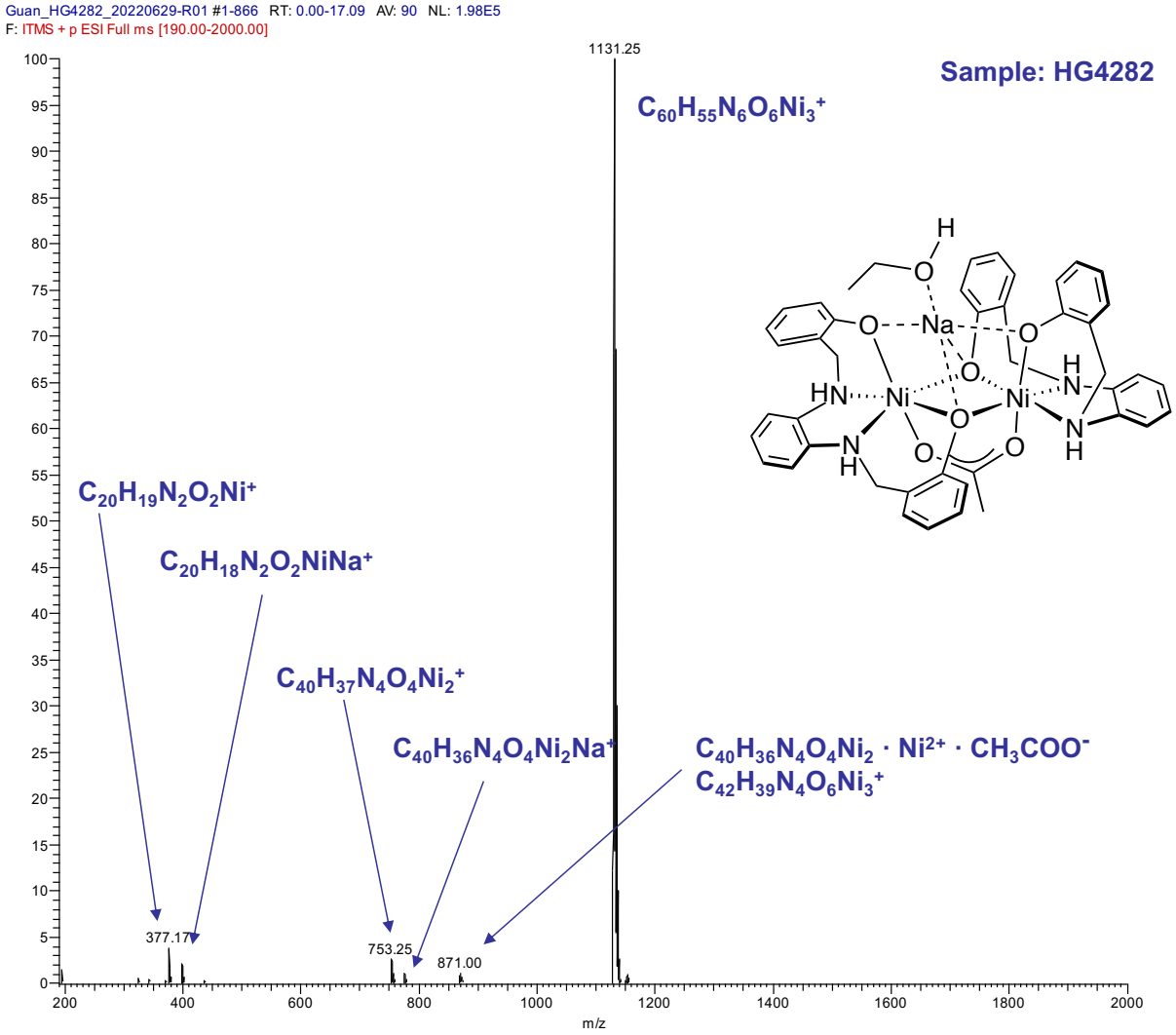


Fig. S5 ESI-MS spectrum of $Na[Ni_2(salophan)_2(OAc)]$•EtOH ($C_{20}H_{18}N_2O_2Ni$ = Ni(salophan))

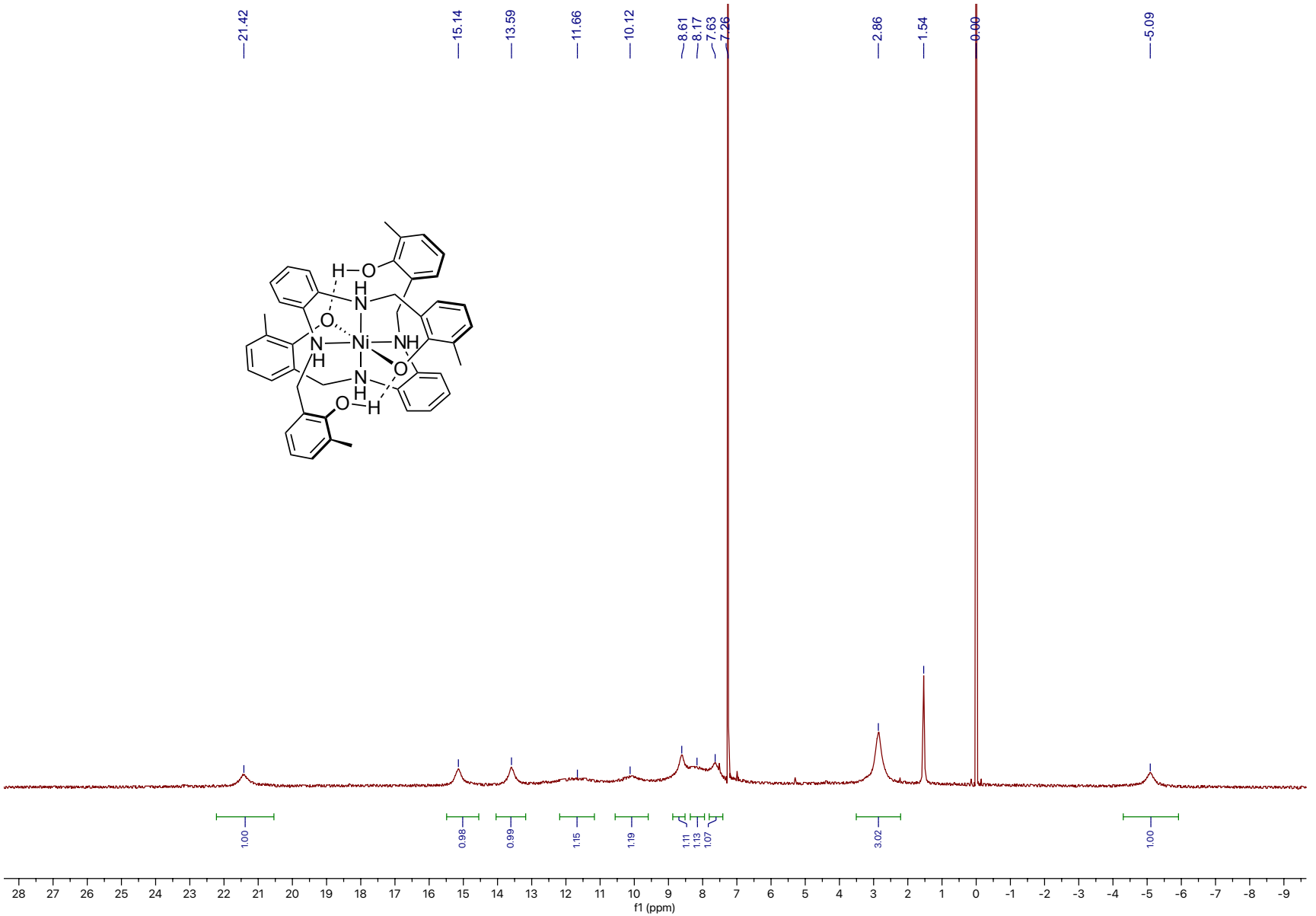


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$, with TMS, 23 °C) spectrum of Ni(Hsalophan_Me)$_2$

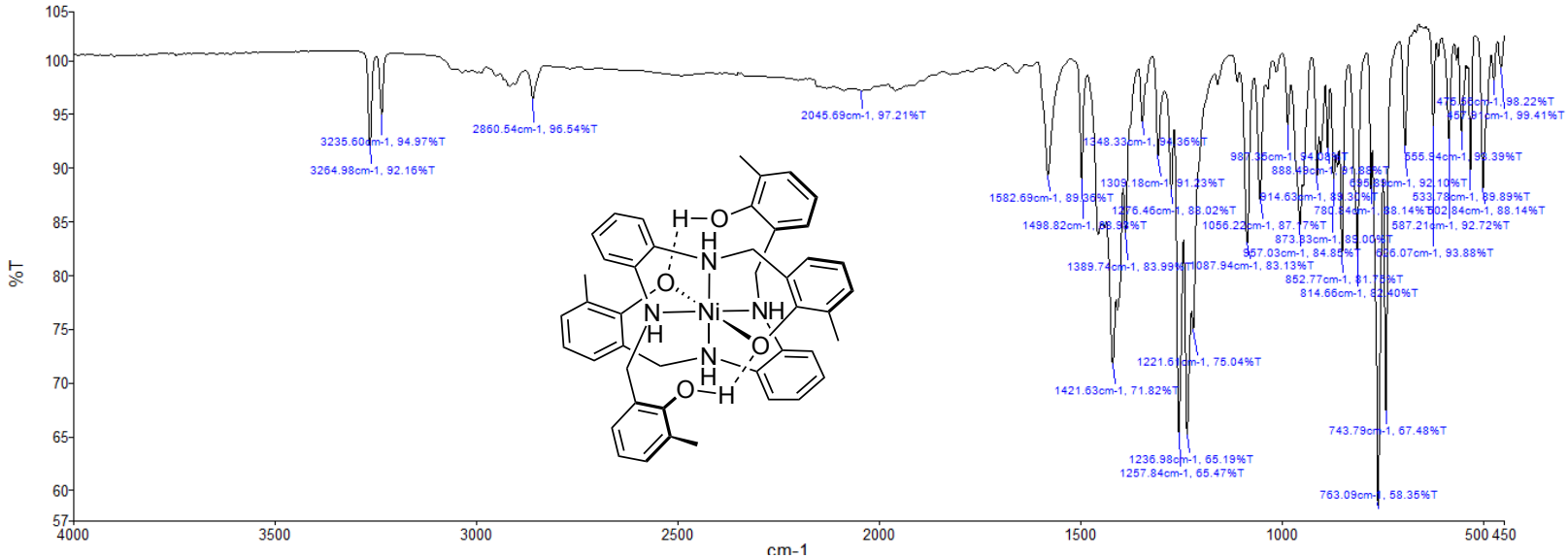


Fig. S7 IR spectrum of Ni(Hsalophan_Me)$_2$ (solid sample)

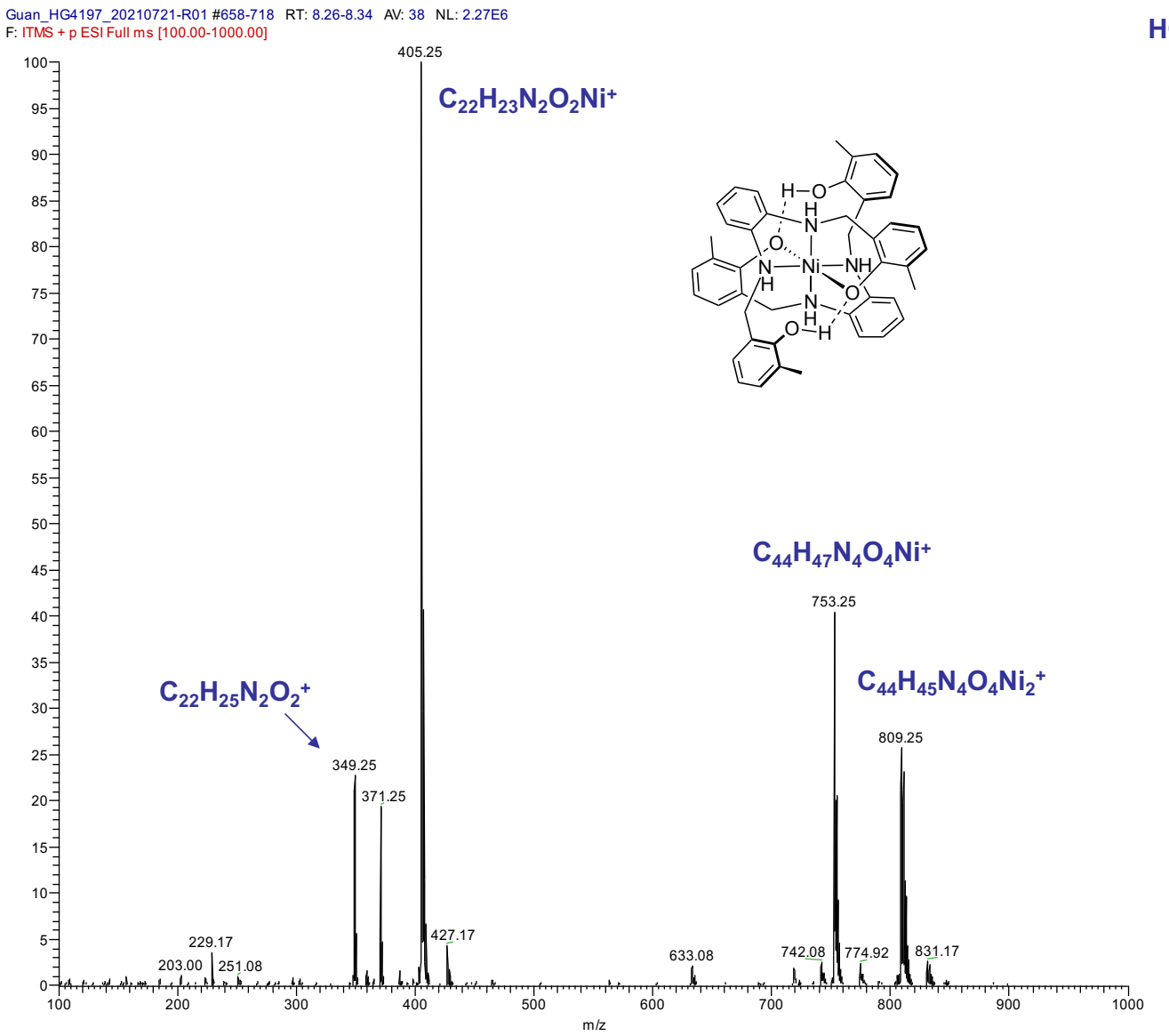


Fig. S8 ESI-MS spectrum of Ni(Hsalophan_Me)$_2$ ($C_{44}H_{46}N_4O_4Ni$ = Ni(Hsalophan_Me)$_2$)

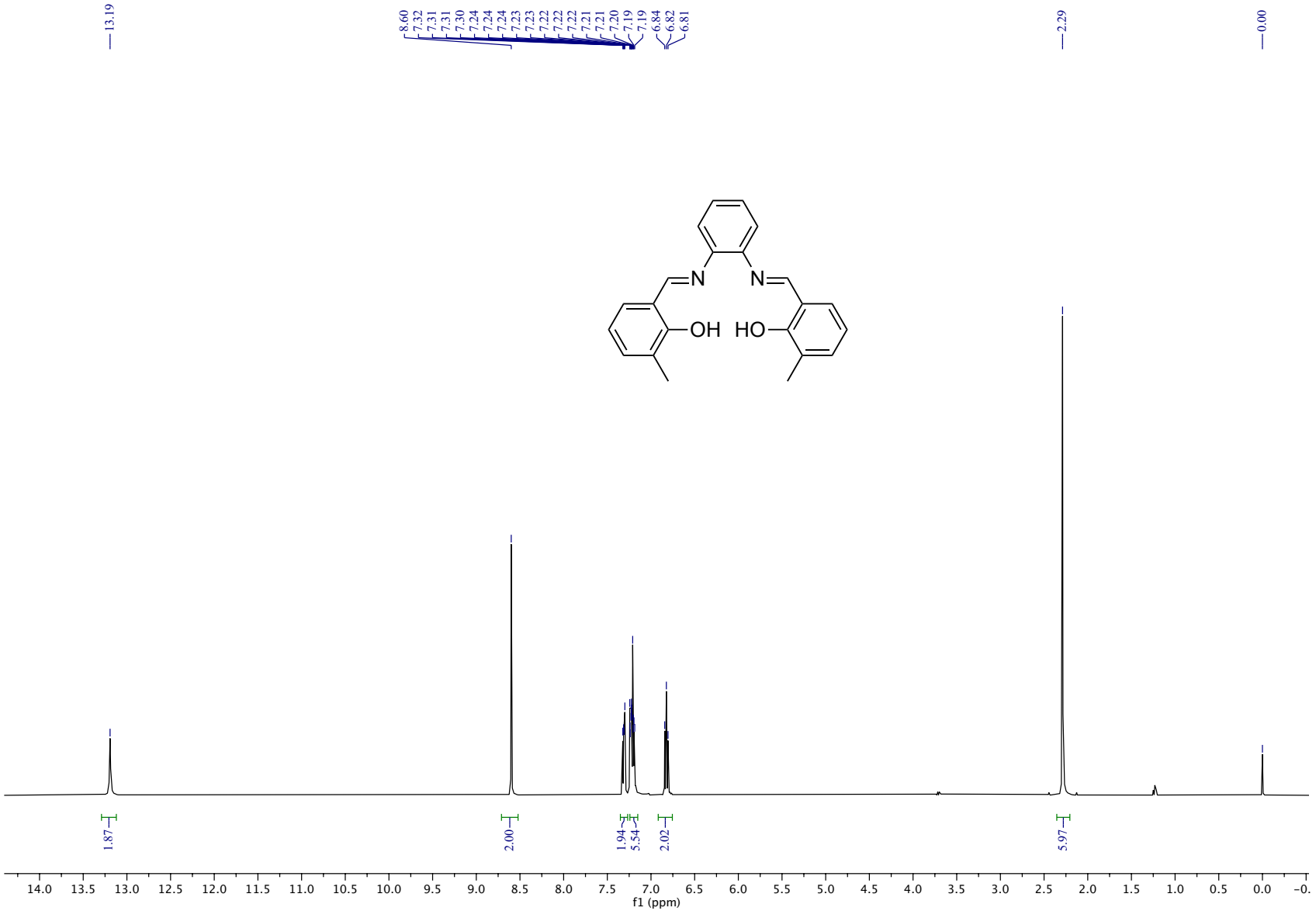


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$, with TMS, 23 °C) spectrum of H_2salophen_Me

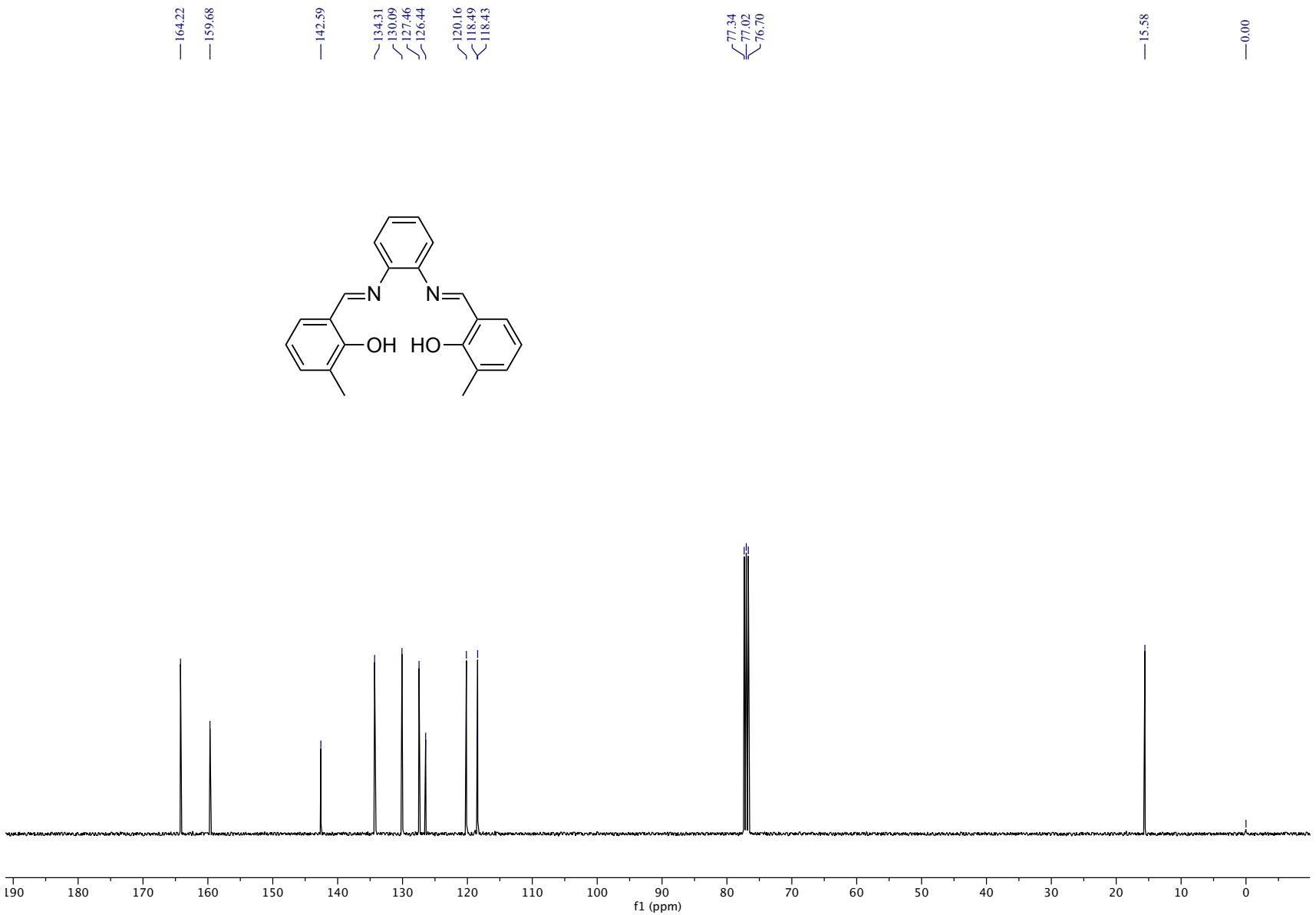


Fig. S10 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, with TMS, 23 °C) spectrum of H_2salophen_Me

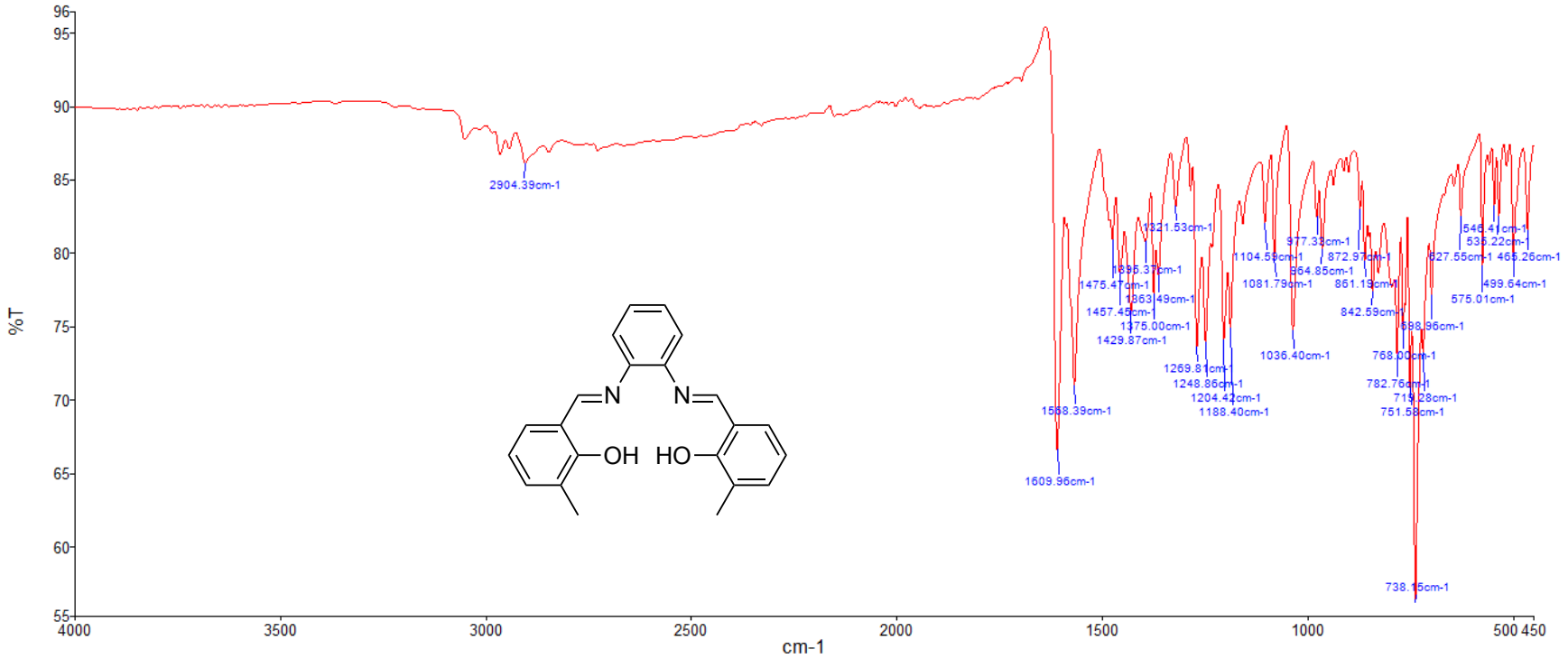


Fig. S11 IR spectrum of H_2salophen_Me (solid sample)

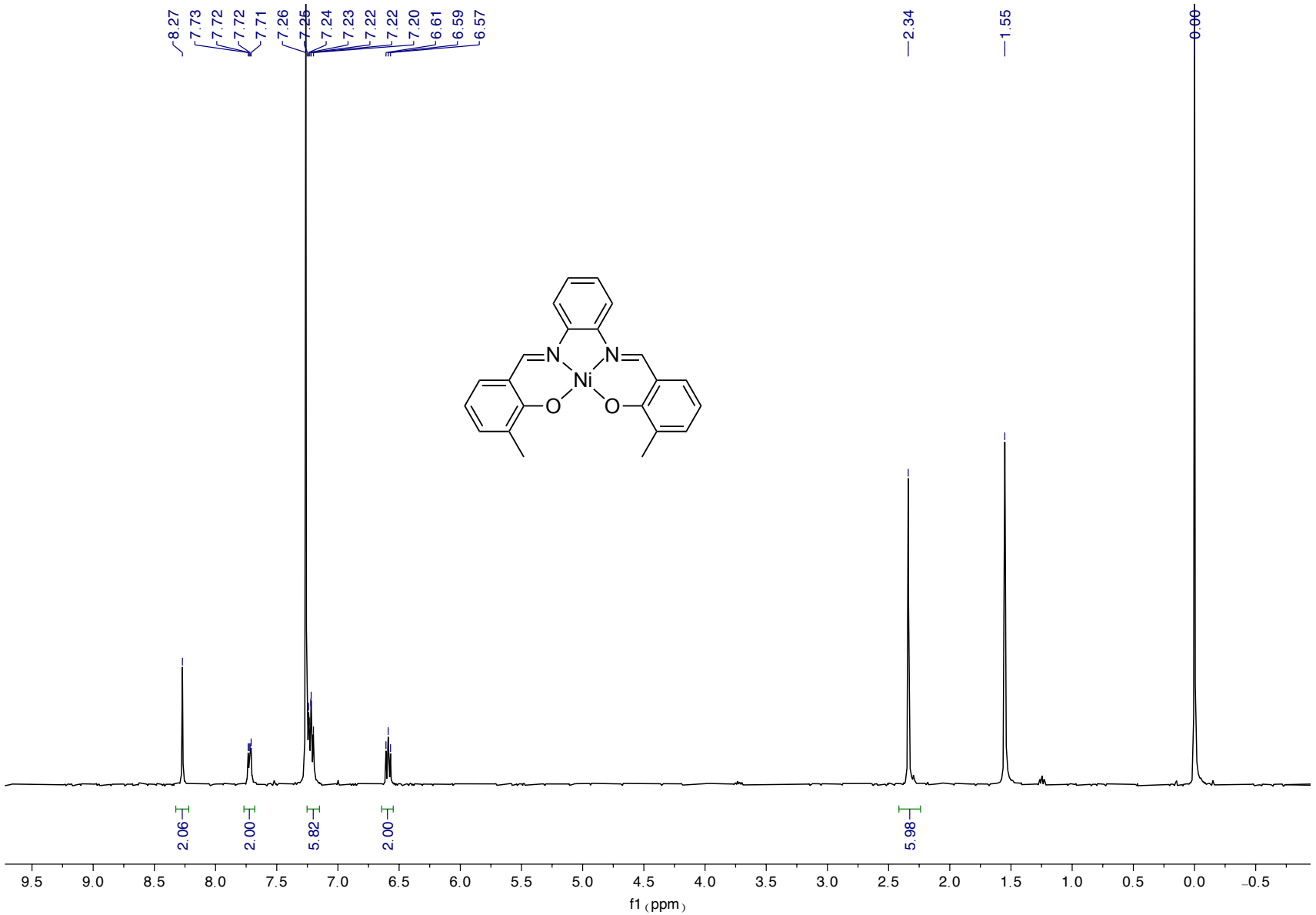


Fig. S12 ^{1}H NMR (400 MHz, $CDCl_3$, with TMS, 23 ^{o}C) spectrum of Ni(salophen_Me)

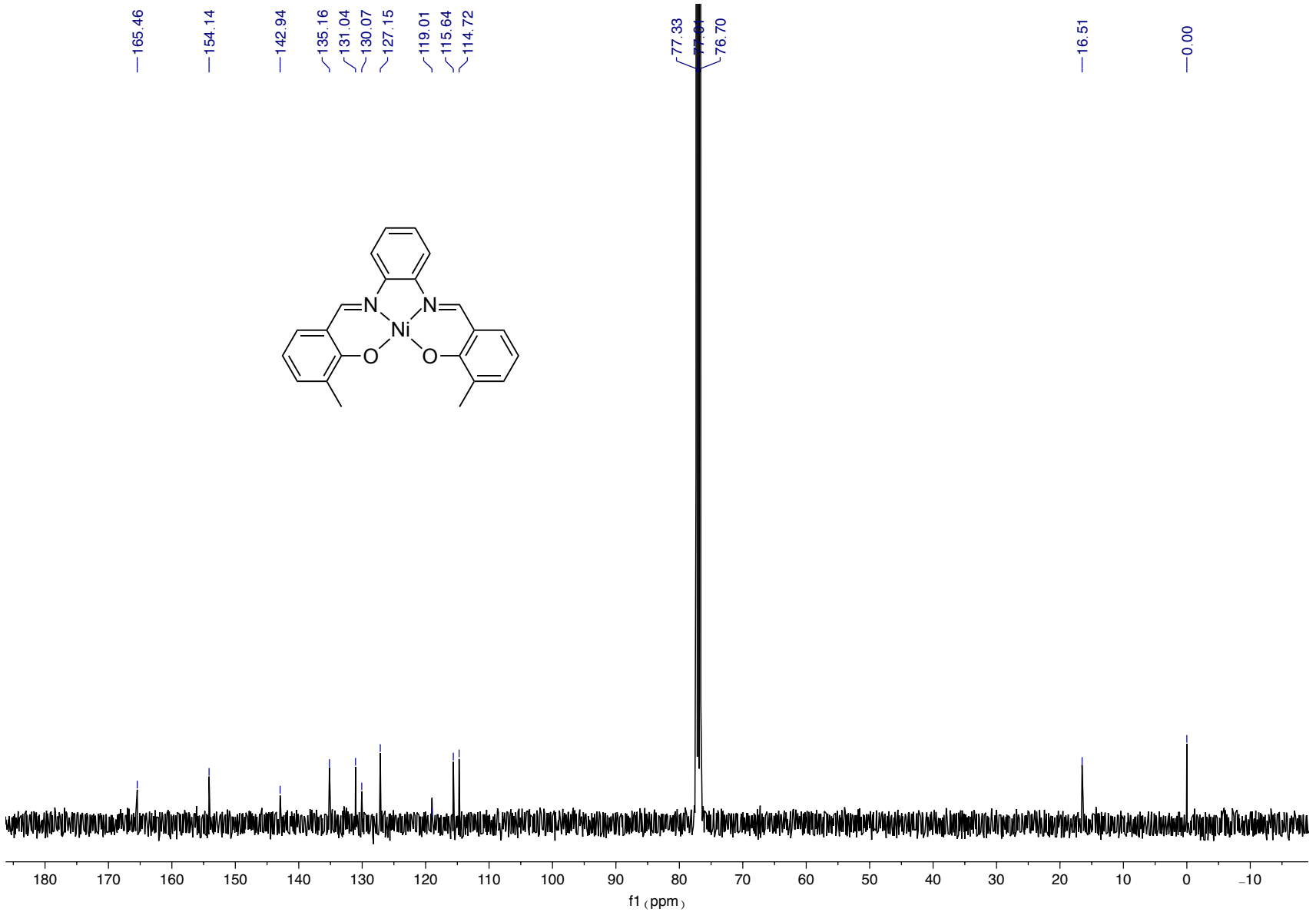


Fig. S13 $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, with TMS, 23 °C) spectrum of Ni(salophen_Me)

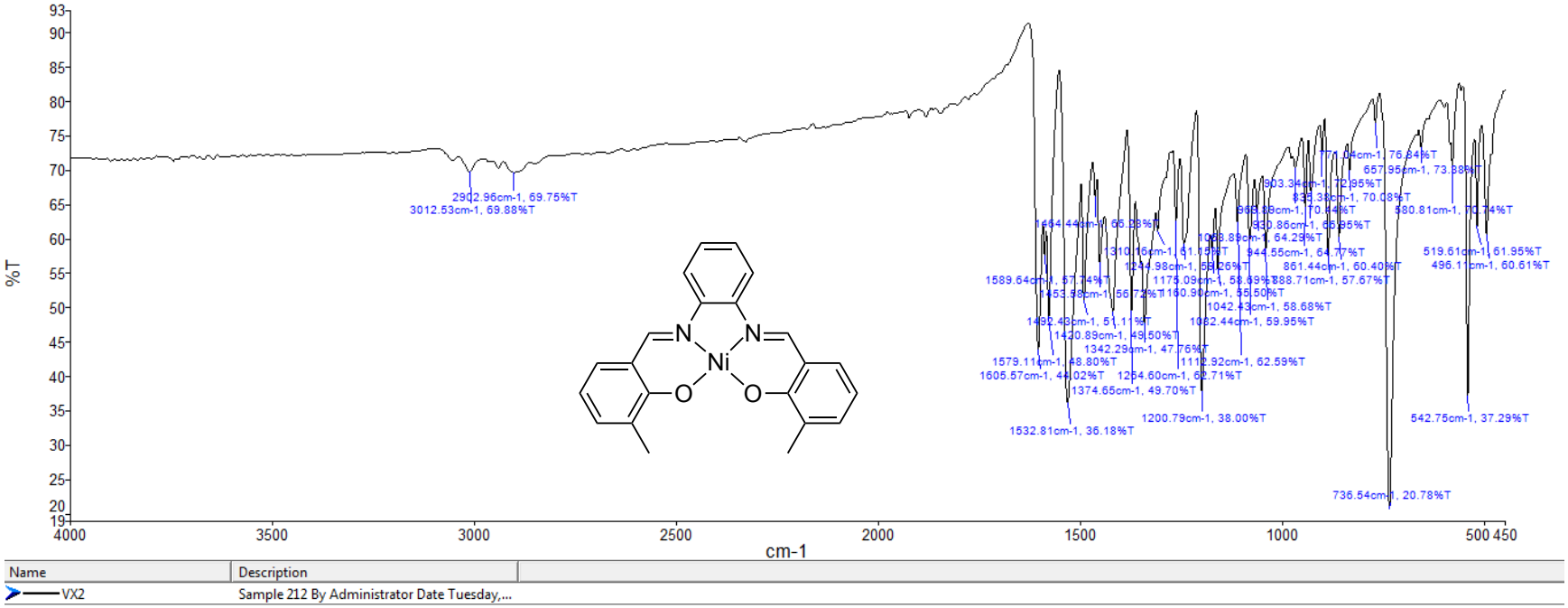


Fig. S14 IR spectrum of Ni(salophen_Me) (solid sample)

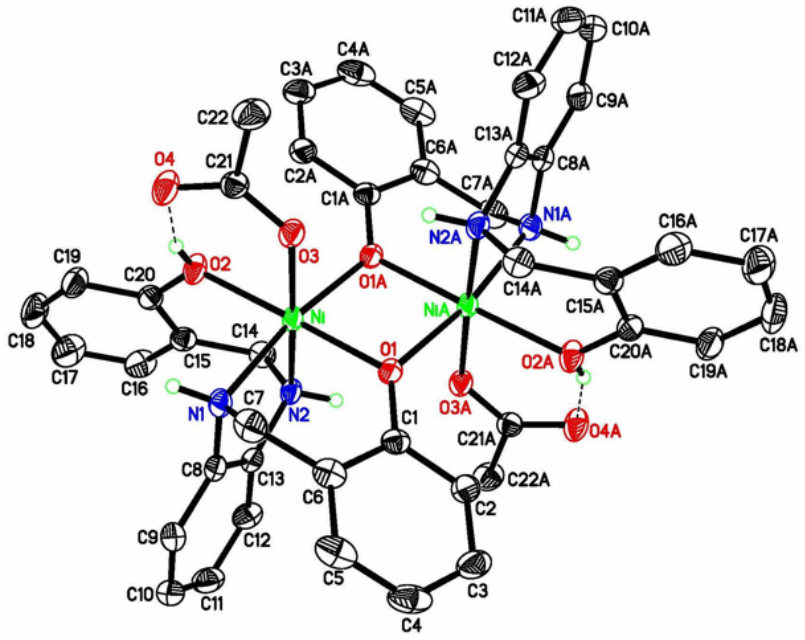


Fig. S15 ORTEP of $Ni_2(Hsalophan)_2(OAc)_2 \bullet 2CH_3COCH_3$ at the 50% probability level. Two co-crystallized acetone molecules and all hydrogen atoms except the ones bound to nitrogen and oxygen are omitted for clarity (intramolecular hydrogen-bonding interactions shown by dashed lines). Selected bond lengths (Å) and angles (deg): Ni−O1 2.0365(13), Ni−O1A 2.0698(12), Ni−O2 2.0786(13), Ni−O3 2.0764(13), Ni−N1 2.0789(16), Ni−N2 2.0667(16), N1−C7 1.492(3), N2−C14 1.493(2), C21−O3 1.260(2) and C21−O4 1.266(2); O1−Ni−O2 178.15(5), O1A−Ni−N1 169.99(6), O3−Ni−N2 176.46(6) and Ni−O1−NiA 97.26(6).

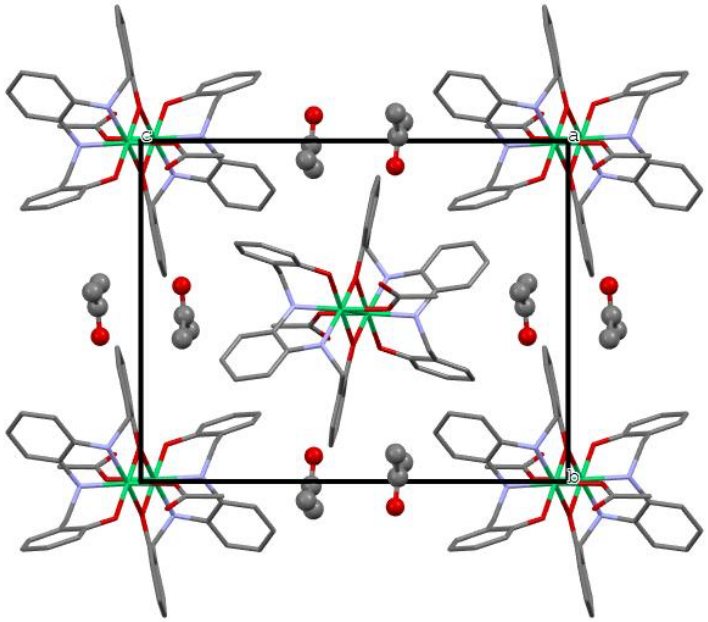


Fig. S16 Packing arrangement within the crystal lattice of $Ni_2(Hsalophan)_2(OAc)_2 \bullet 2CH_3COCH_3$ showing the relationship of the neighboring molecules and the solvent acetone (shown as ball-n-stick). H-atoms omitted for clarity.

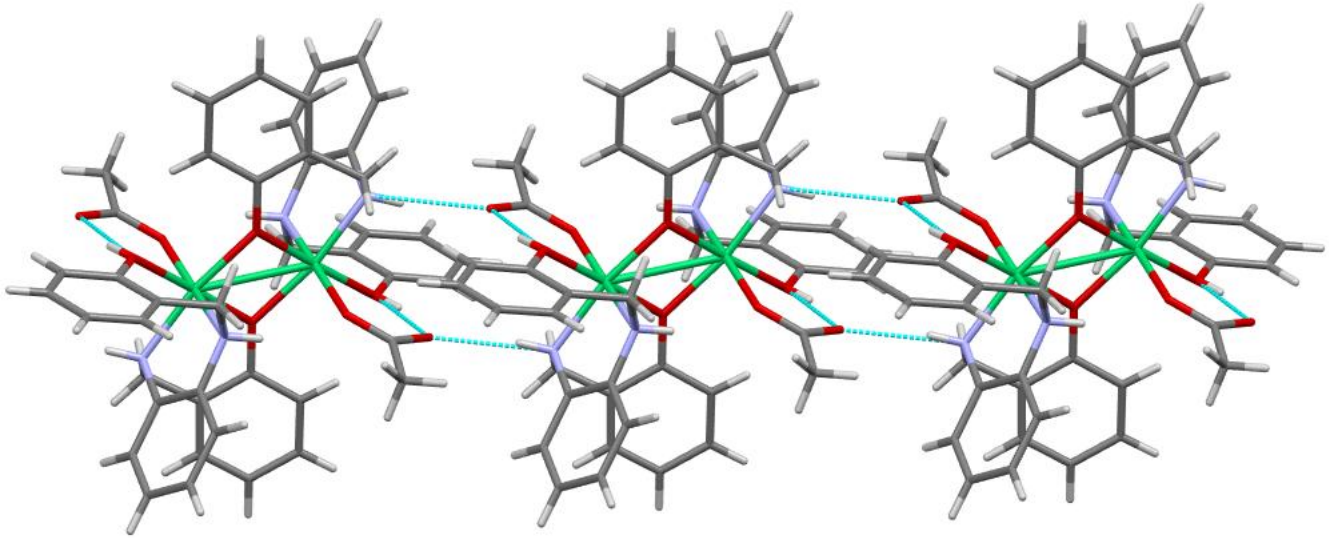


Fig. S17 Extended packing of $Ni_2(Hsalophan)_2(OAc)_2 \bullet 2CH_3COCH_3$ showing the NH…O intermolecular interactions between neighboring molecules making up the crystal (dashed lines between molecules). The OH…O intramolecular interactions are also shown as dashed lines.

Intramolecular and Intermolecular H-bonds:

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(3)...O(4)	0.77(2)	1.74(2)	2.4788(18)	160(3)
N(2)-H(2)...O(3)#1	0.85(3)	2.31(3)	3.118(2)	160(2)
N(1)-H(1)...O(4)#2	0.84(2)	2.18(2)	2.985(2)	160(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1

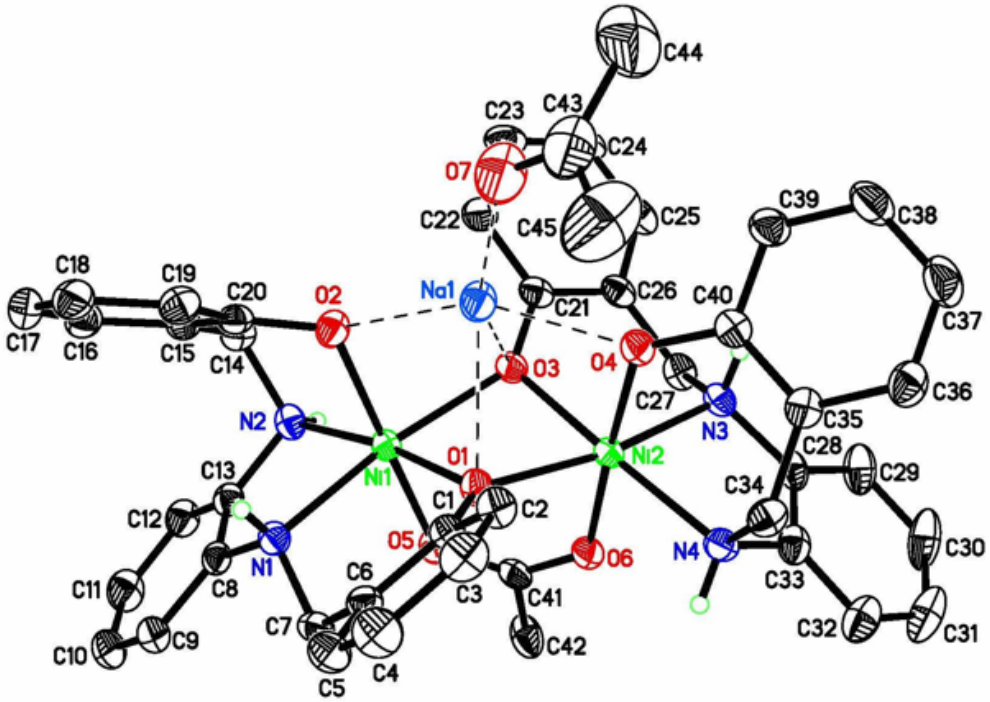


Fig. S18 ORTEP of $Na[Ni_2(salophan)_2(OAc)]\bullet 4CD_3COCD_3$ at the 50% probability level. Three co-crystallized CD_3COCD_3 molecules and all carbon-bound hydrogen atoms are omitted for clarity (sodium-oxygen interactions shown as dashed lines). Selected bond lengths (Å) and angles (deg): Ni1−O1 2.0456(16), Ni1−O2 2.0525(16), Ni1−O3 2.1181(15), Ni1−O5 2.0489(16), Ni2−O1 2.0805(15), Ni2−O3 2.0491(16), Ni2−O4 2.0363(16), Ni2−O6 2.0462(16), Ni1−N1 2.1193(19), Ni1−N2 2.105(2), Ni2−N3 2.1064(19), Ni2−N4 2.092(2), N1−C7 1.490(3), N2−C14 1.498(3), N3−C27 1.489(3), N4−C34 1.497(3), C41−O5 1.256(3) and C41−O6 1.259(3); O1−Ni1−N2 171.97(7), O3−Ni1−N1 167.01(7), O2−Ni1−O5 174.01(7), O3−Ni2−N4 173.75(7), O1−Ni2−N3 169.39(7) and O4−Ni2−O6 177.42(7).

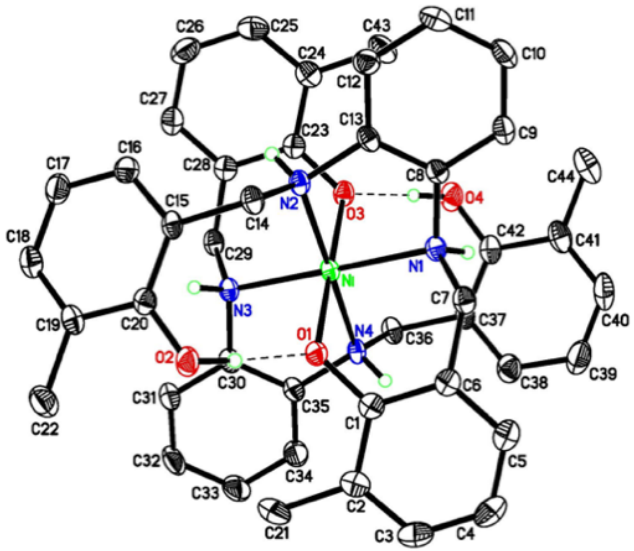


Fig. S19 ORTEP of Ni(Hsalophan_Me)$_2$•2CH_3COCH_3 at the 50% probability level. Two co-crystallized acetone molecules and all carbon-bound hydrogen atoms are omitted for clarity (hydrogen-bond interactions shown as dashed lines). Selected bond lengths (Å) and angles (deg): Ni−O1 2.0754(13), Ni−O3 2.0808(13), Ni−N1 2.0956(16), Ni−N2 2.1252(16), Ni−N3 2.1042(16), Ni−N4 2.1353(16), N1−C7 1.504(2), N2−C14 1.496(2), N3−C29 1.502(2) and N4−C36 1.498(2); O1−Ni−O3 178.98(5), N1−Ni−N3 179.06(7) and N2−Ni−N4 179.36(6).

Intramolecular H-bonds:

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(5)...O(1)	0.89(2)	1.65(2)	2.5369(19)	175(2)
O(4)-H(6)...O(3)	0.89(2)	1.65(2)	2.5374(19)	175(2)

The N-H hydrogens do not participate in hydrogen bonding.

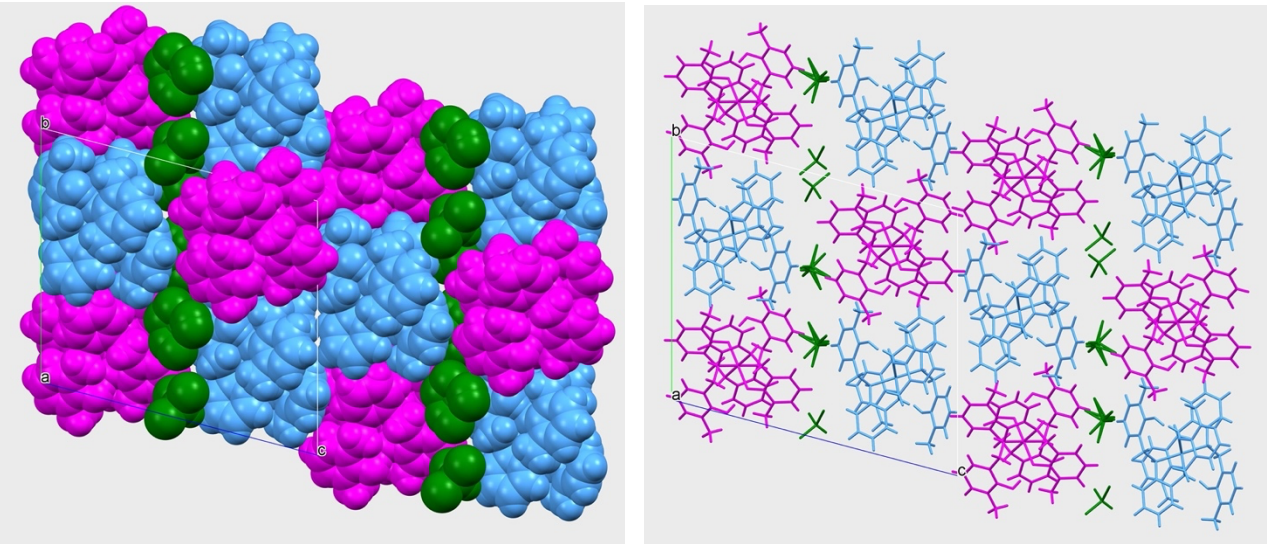


Fig. S20 Crystal packing of Ni(Hsalophan_Me)$_2$•CHCl$_3$. There are two independent molecules (shown in pink and blue) that crystallize along with two chloroform molecules (shown in green) in the lattice that make up the crystal. Selected bond lengths (Å) and angles (deg): Molecule A: Ni1−O1A 2.0754(13), Ni1−O2A 2.0822(13), Ni1−N1A 2.1130(16), Ni1−N2A 2.1315(17), Ni1−N3A 2.1076(16), Ni1−N4A 2.1288(17), N1A−C7A 1.508(2), N2A−C14A 1.495(2), N3A−C29A 1.508(2) and N4A−C36A 1.499(2); O1A−Ni1−O2A 179.15(5), N1A−Ni1−N3A 179.25(6) and N2A−Ni1−N4A 179.47(7); Molecule B: Ni2−O1B 2.0706(14), Ni2−O2B 2.0605(13), Ni2−N1B 2.1080(17), Ni2−N2B 2.1416(16), Ni2−N3B 2.1131(17), Ni2−N4B 2.1447(17), N1B−C7B 1.504(3), N2B−C14B 1.500(2), N3B−C29B 1.505(2) and N4B−C36B 1.494(3); O1B−Ni2−O2B 179.01(6), N1B−Ni2−N3B 179.53(7) and N2B−Ni2−N4B 179.56(6).

Intramolecular H-bonds:

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3A)-H(5)...O(1A)	0.87(2)	1.66(3)	2.527(2)	176(2)
O(4A)-H(6)...O(2A)	0.84(2)	1.69(3)	2.529(2)	173(3)
O(3B)-H(11)...O(1B)	0.82(2)	1.69(3)	2.506(2)	173(3)
O(4B)-H(12)...O(2B)	0.87(2)	1.67(3)	2.524(2)	167(3)

The N-H hydrogens do not participate in hydrogen bonding.

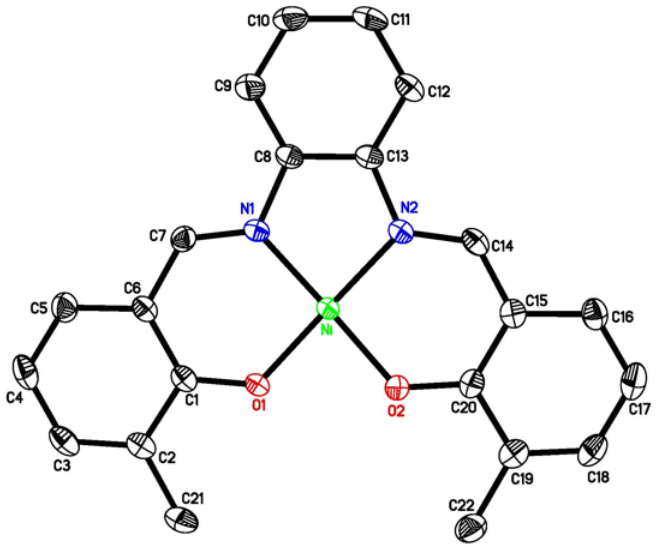


Fig. S21 ORTEP of Ni(salophen_Me) at the 50% probability level. All carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni−O1 1.8444(14), Ni−O2 1.8397(15), Ni−N1 1.8537(18), Ni−N2 1.8579(17), N1−C7 1.302(3) and N2−C14 1.306(3); O1−Ni−N2 177.89(7), O2−Ni−N1 177.19(7), O1−Ni−O2 83.99(6) and N1−Ni−N2 86.00(8).

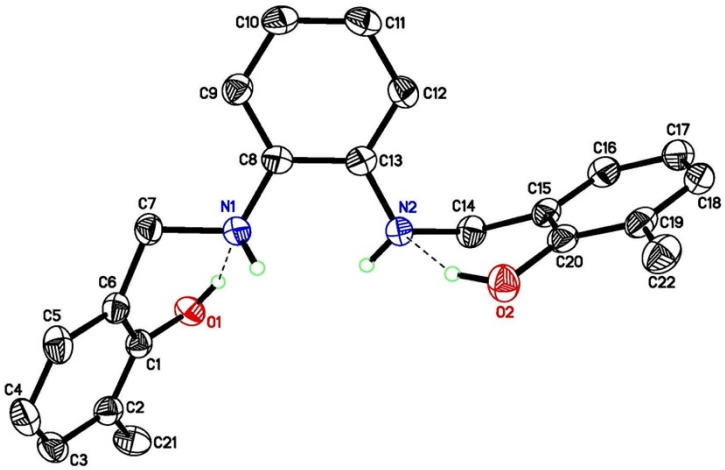
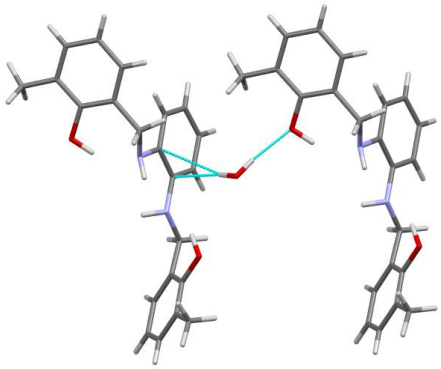


Fig. S22 (left) ORTEP of H_2salophan_Me•H_2O at the 50% probability level. Co-crystallized water molecule and all carbon-bound hydrogen atoms are omitted for clarity (intramolecular hydrogen-bonding interactions shown as dashed lines). Selected bond lengths (Å): N1−C7 1.472(2), N1−C8 1.424(2), N2−C13 1.412(2) and N2−C14 1.472(2).



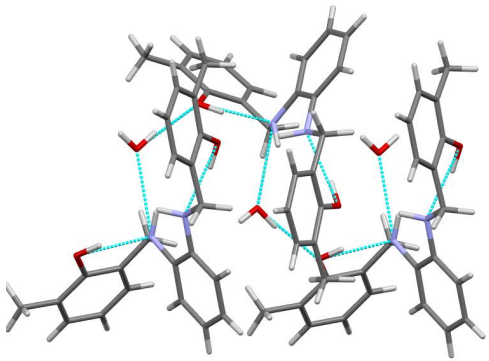
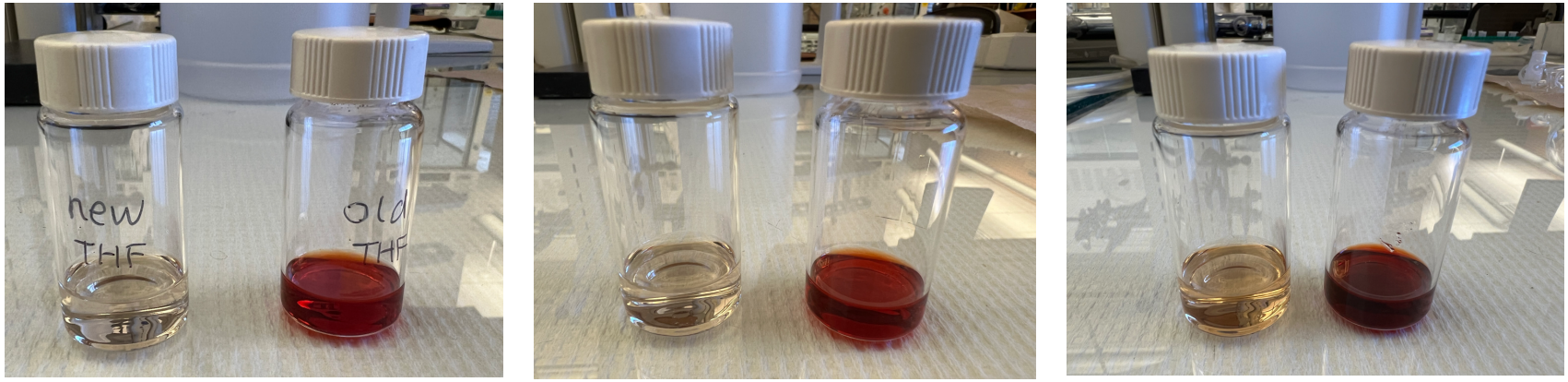


Fig. S23 (right) Additional bonding information for H_2salophan_Me•H_2O. The complex and the lattice water participate in NH…O and OH…O hydrogen bonding interactions (see table) as well as weak interactions with the edge of an aromatic ring (H2W…C8 = 2.56Å, H2W…C13 = 2.75Å) (interactions show as dashed lines)

Intramolecular and Intermolecular H-bonds:

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(1)	0.90(3)	2.00(3)	2.809(2)	148(2)
O(2)-H(2)...N(2)	0.93(3)	1.86(3)	2.695(2)	148(2)
N(1)-H(3)...O(1)#1	0.91(2)	2.19(2)	3.099(2)	175(2)
N(2)-H(4)...O(1W)#2	0.88(2)	2.31(2)	3.067(2)	144(2)
O(1W)-H(1W)...O(2)	0.88(4)	1.99(4)	2.862(2)	172(3)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1,z #2 x-1/2,-y+1,z



(A) 5 min after mixing **(B) 10 min after mixing** **(C) 1 h after mixing**

Figure S24 Sensitivity of Ni(Hsalophan_Me)$_2$ to the peroxide in THF

Experimental details: 3 mg of Ni(Hsalophan_Me)$_2$ was dissolved in 3 mL of THF from two different sources. The "new THF" in the left vial has a low peroxide level (close to 0 ppm), whereas the "old THF" in the right vial has a high peroxide level (50 ppm). The peroxide level was checked by XploSen PS^{TM} peroxides detection strips.
Caution: solvents with a high peroxide level are a safety hazard and should be disposed appropriately and promptly.