A Coordination-Assisted General Approach to Nickel-Based Nano Metallogels

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Supplementary Information

Experimental :

In a typical gel formation reaction, a methanolic (0.3 mL, 7.39 mmol) solution of $NiCl_2.6H_2O$ (18 mg, 0.076 mmol) in a screw-cap vial was added *N*-methylmorpholine (**L2**: 0.2 mL, 1.82 mmol). The glass vial was left at room temperature. After 2 min a sea-green coloured dense gel was formed, which was confirmed by inverting the vial (Figure 1, see manuscript). The **MOG-1** and **MOG-2** can also be prepared in bulk. The large amount of gel prepared from 25 g of $NiCl_2.6H_2O$ with **L1** and 12.5 g with **L2** in a 250 mL round-bottom flask and a 100 mL conical flask respectively is stable to inversion (Figure I). It appears that these gels may be easily prepared in a much larger quantity without any special precautions.

Figure I: The large amount of gel (**MOG-1** and **MOG-2**) made from $NiCl_2.6H_2O$ and **L1** and **L2** respectively

Sol−Gel Transformations of MOG-2 by Chemical Stimuli:

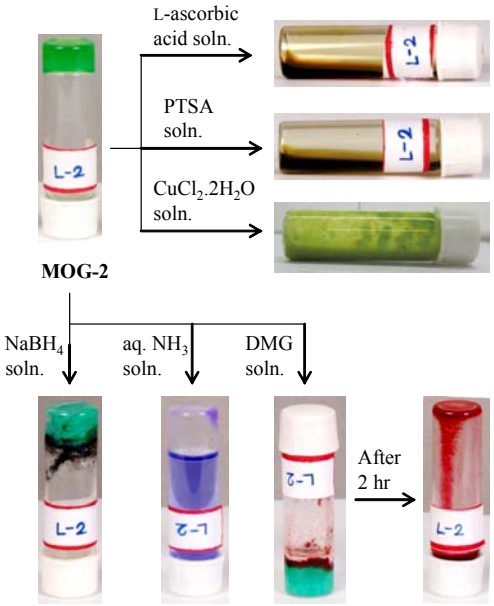

Figure II: Disruption of MOG-2 by external chemical stimuli such as L-ascorbic acid, PTSA, $CuCl_2.2H_2O$, $NaBH_4$, aq. NH_3 and DMG solution

Microscopy Study:

Still photographs were taken with a NIKON D60 digital camera.

The **MOG-1** and **MOG-2** have been analyzed using various types of microscopy to get some visual insights into their morphology. Supramolecular 3D aggregation of the gel was investigated with a field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and polarized optical microscope (POM).

(a) Field Emission Scanning Electron Microscope (FESEM)

A field emission scanning electron microscope (FESEM, Zeiss, Supra-40) operating at 5−10 kV was used to obtain the micrograph. For electron micrographs, the gel sample solution was placed on the glass pieces, allowed to dry at room temperature, and then dried in desiccators for 24 h. A layer of gold was sputtered on top to make a conducting surface, and finally, the specimen was transferred into the microscope. FESEM images of xerogel (dried gel) of **MOG-1** shows a crystalline nature (Figure III). In the case of dried xerogel **MOG-2** shows a lamellar morphology was observed (Figure IV). This could be due to the presence of different hydrophobic group in the side arm of gelator molecule.

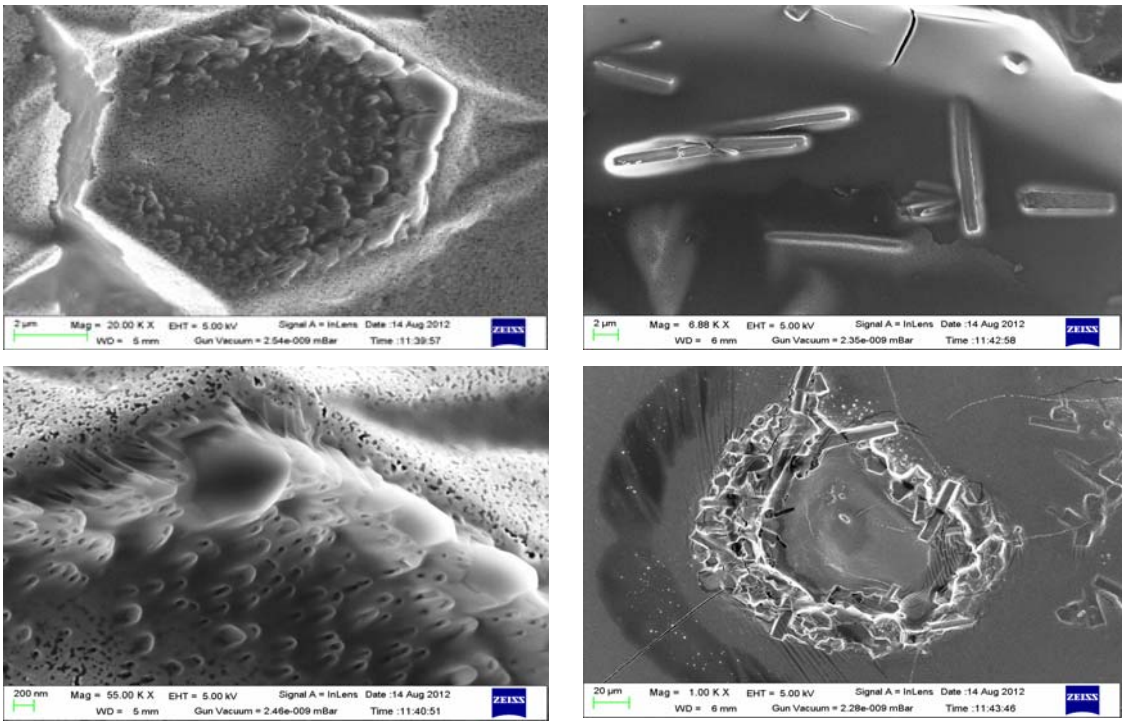

Figure III: FESEM images of **MOG-1**

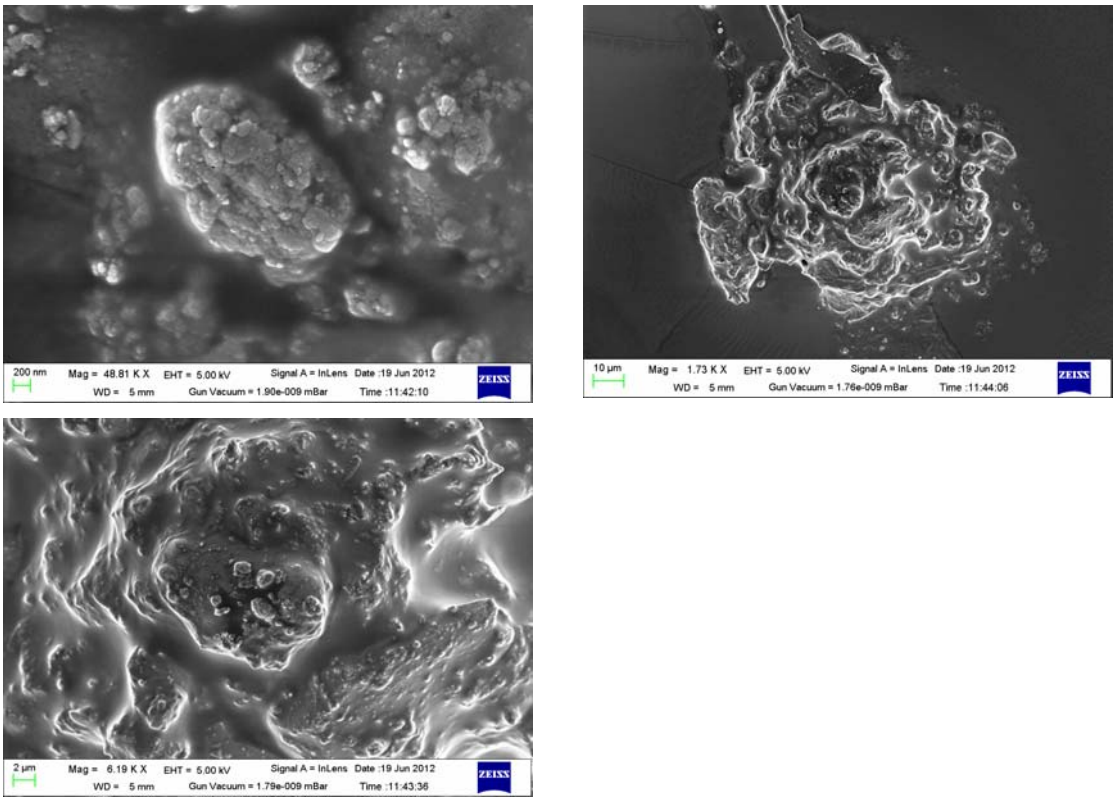

Figure IV: FESEM images of **MOG-2**

(b) Transmission Electron Microscope (TEM).

The gel materials were examined by a transmission electron microscope (FEI-TECNAI G2 20S-TWIN, Type-5022/22). The sample was prepared by placing a drop of gel on a carbon-coated copper grid. From transmission electron microscopy (TEM), the structure of the **MOG-1** and **MOG-2** are composed of recently discovered nanoscale metal-organic particles (NMOPs) (Figure V and VI). The TEM image of **MOG-1** shows the particle in the gel network.

(c) Polarized Optical Microscope (POM).

The polarizing optical light micrographs for the samples were obtained from a LEICA DMLM (Germany) optical microscope by transmitted light under crossed Nicol and fitted with JVC-KY-F550E imaging system. A drop of the gelatinous samples from the 0.1 equivalent sample vial was placed on the microscope slide and placed under the microscope. The elongated fibers form a gel network is clearly visible in the POM images (Figure VII and VIII).

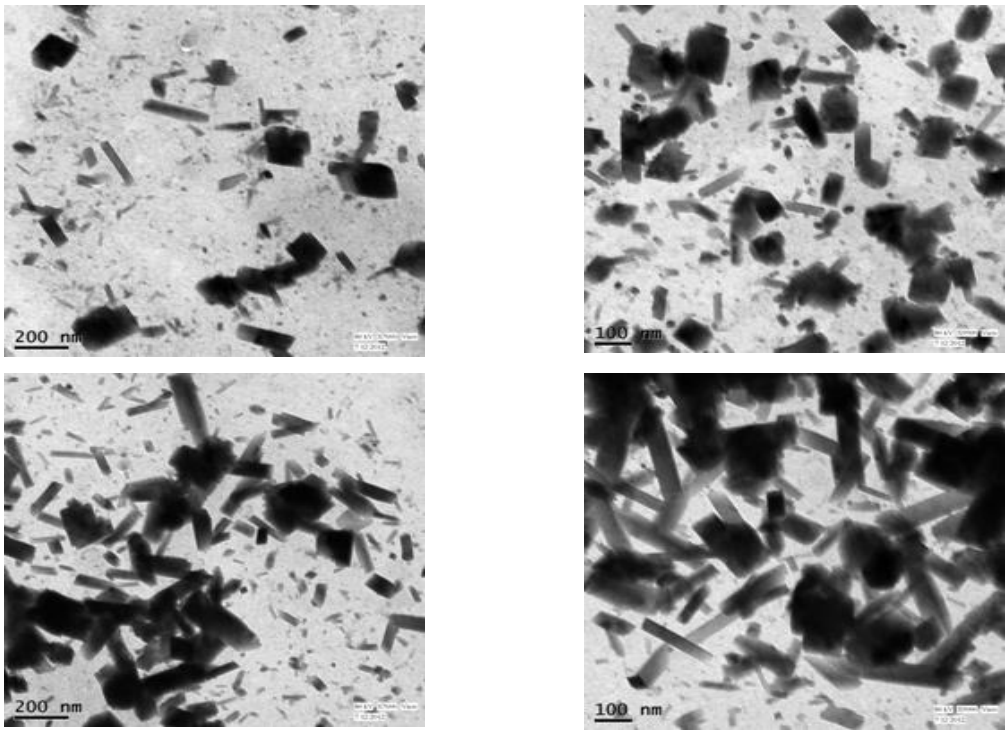

Figure V: TEM images of **MOG-1**

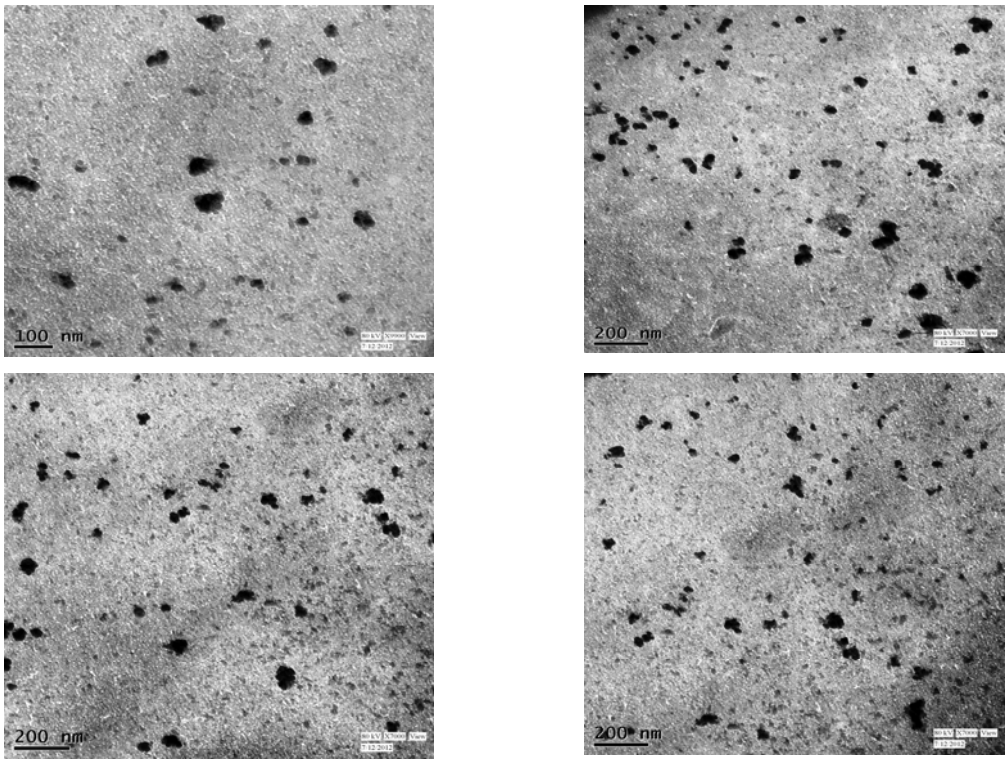

Figure VI: TEM images of **MOG-2**

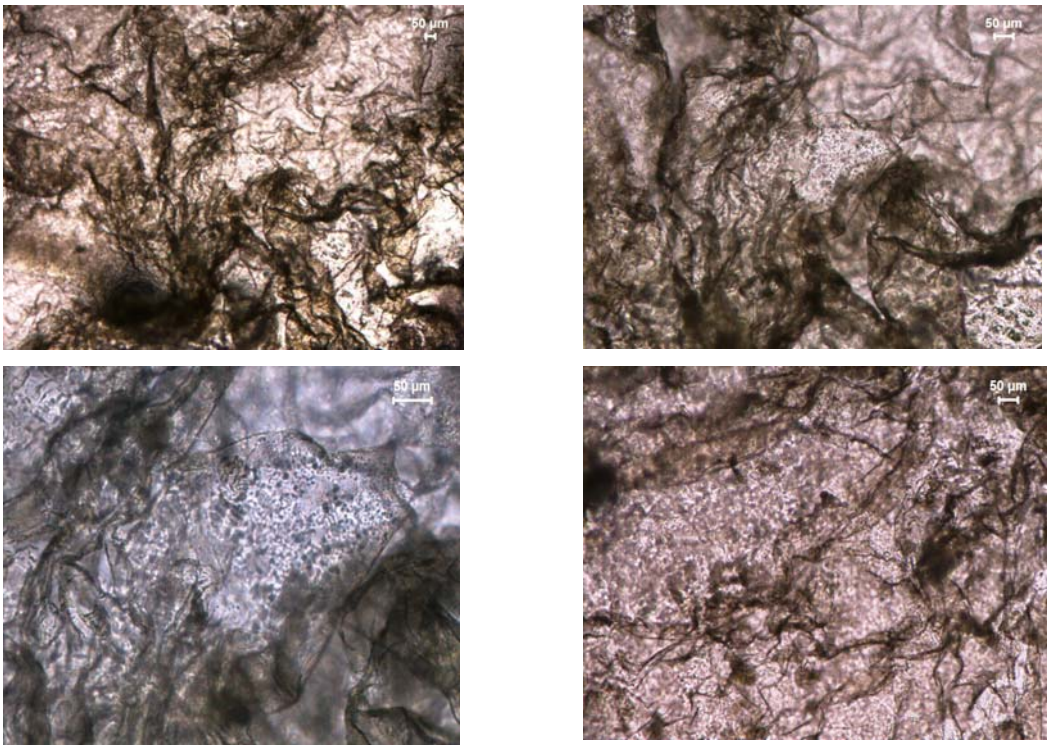

Figure VII: POM images of **MOG-1**

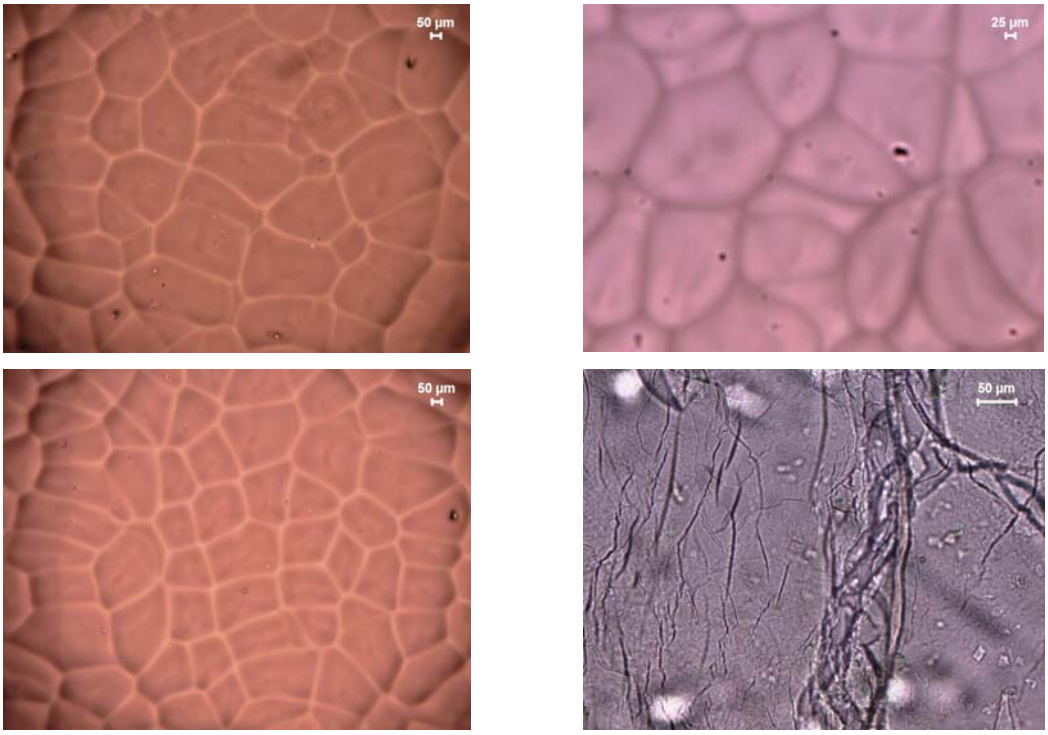

Figure VIII: POM images of **MOG-2**

Powder XRD:

A small amount of xerogel was taken in to sample holder and the reflectance was measured. Powder XRD experiments were carried out using an X-ray diffractometer (Bruker AXS, Diffraktometer D8) with target Cu. The **MOG-1** and **MOG-2** were dried and the xerogels were used for powder XRD. First sharp peaks were found at 2θ = 12.4 degree for **MOG-1** and 2θ = 12.6 degree for **MOG-2**, suggests an ordered arrangement of gelators in the fibers (Figure 5 in the manuscript).

Kinetics study of gel formation:

We tried to investigate the kinetics of gel formation by UV spectroscopy with an aid of Shimadzu UV spectrophotometer (model no. UV 2450). All the **MOGs** mentioned above can well be characterized by their own colors in visible region. As a representative example, *N*-methylmorpholine was chosen for this purpose due to its sluggishness during gel formation at CGC. From the absorbance versus wavelength plot recorded by UV-visible spectrophotometer (Figure IX), it was quite evident that initially, there might be an advent of either or both of pentagonal bi-pyramidal and square planer species which is attributed to shift of λ_{max} towards higher wavelength (480 nm) eliciting yellowish coloration of mixture. Initially the intensity of higher wave-length band at 480 nm increases steadily and reaches to its maximum absorbance after 600 seconds, then gradually decreases for a period of time (in between the time interval of 600 to 1450 seconds) and finally started to collapse as a shoulder

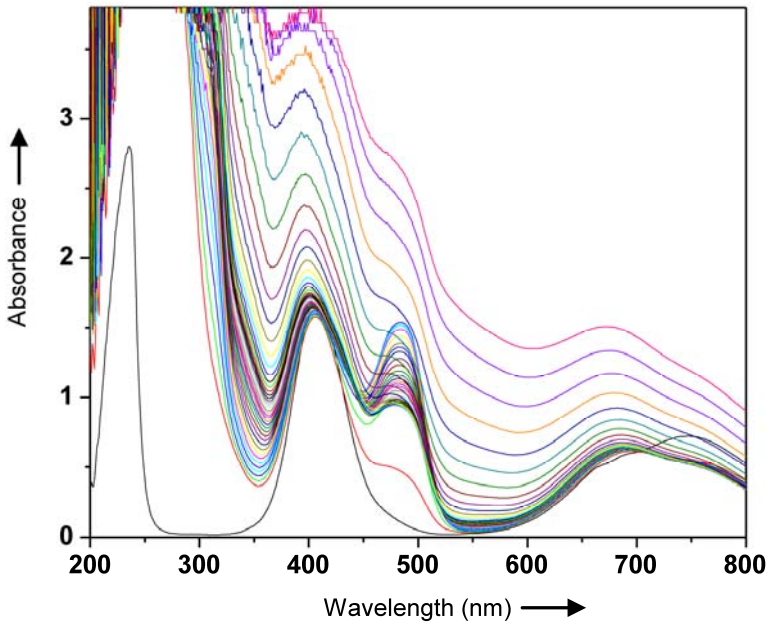

Figure IX: Wavelength vs absorbance plot for monitoring the gelation of $NiCl_2.6H_2O$ and N-methylmorpholine (**L2**) in MeOH.

peak of the main transformed peak at a lower λ_{max} 390 nm (after 1450 seconds) (Figure X). At this point of time gel formation was over and λ_{max} 390 nm corroborates to octahedral or tetrahedral geometry of species therein.

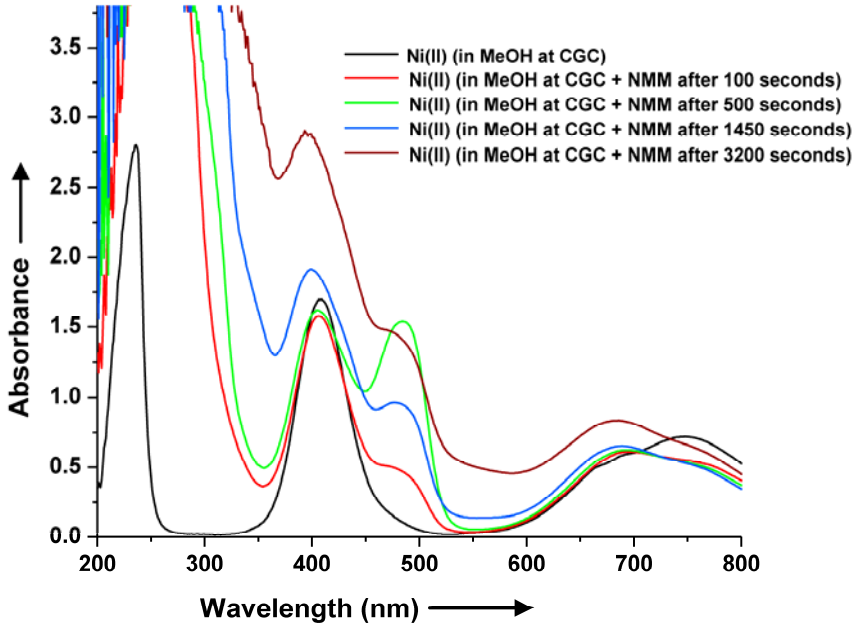

Figure X: Wavelength vs. absorbance plot in UV-Vis spectrometer at different time intervals, indicating the kinetics of gel formation through intermediate species.

Computational Study:

There are only limited information available to propose the molecular arrangement in the gel, either experimental evidence or literature reports. Therefore we have modelled complexes containing Cl^-, H_2O, MeOH, OMe^- and Et_3N as ligands. The possible geometries of hexa-, penta- and tetra-coordinate complexes are optimized. Complexation Energy (CE) is calculated as the difference between the energy of optimized geometries of Ni^{2+} complexes and the sum of the energies of the constituent free ligands (fully optimized) and the Ni^{2+} ion. We have also computed the isodesmic energies for various ligand exchange reactions. All the geometries were initially optimized with BP86/def2-SVP and further reoptimized with B3LYP/def2-TZVP. All the energies discussed in the text are from B3LYP calculations. Some of the geometries that were located at BP86 were not stable in B3LYP (See discussion below).

A. Complexeation Energy:

Considering Cl^-, OMe^-, MeOH, H_2O, Et_3N as ligands, we computed the complexation energy in order to understand the stability of the complexes formed from these ligands (Table 1). Where ever applicable, cis, trans forms were considered. Following general observation can be made: Highest CE was found for $Ni(OMe)_2(MeOH)_4$ (Figure XI) and the lowest CE for $Ni(Cl)_2(Et_3N)_2$. Methoxy ions produced by amine and methanol are found to be very efficient in replacing chloride ions. MeOH is a better ligand than Et_3N.

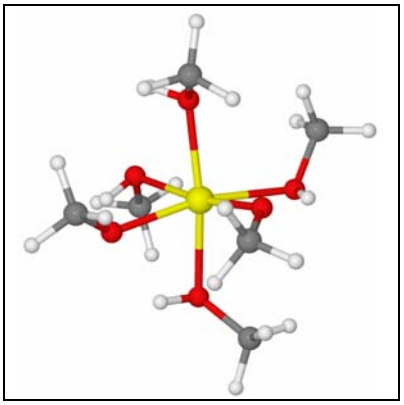

Figure XI: Optimized geometry of *cis*-$Ni(MeO)_2(MeOH)_4$ at B3LYP-D3/def2-TZVP level of theory

Table 1: Complexation Energies of the complexes in decreasing order.

Complex	Isomers	CE(kcal/mol)
$Ni(OMe)_2(MeOH)_4$	cis	-795.73
$Ni(OMe)_2(MeOH)_4$	trans	-793.56
$Ni(OMe)_2(Et_3N)_2$	Tetrahedral	-772.82
$Ni(Cl)_2(MeOH)_4$	trans	-747.30
$Ni(Cl)(OMe)(Et_3N)_2$	tetrahedral	-745.85
$Ni(Cl)_2(MeOH)_4$	cis	-741.40
$Ni(Cl)_2(H_2O)_2(MeOH)_2$	all-trans	-740.96
$Ni(Cl)_2(H_2O)_2(MeOH)_2$	trans- Cl^-,cis-H_2O,cis-MeOH	-738.58
$Ni(Cl)_2(H_2O)_2(MeOH)_2$	all-cis	-736.52
$Ni(Cl)_2(H_2O)_2(MeOH)_2$	cis-MeOH, cis- Cl^-, trans-H_2O	-736.30
$Ni(Cl)_2(MeOH)_2Et_3N$	Sq-pyramidal, Et_3N-axial	-733.79
$Ni(Cl)_2(H_2O)_4$	cis	-733.46
$Ni(Cl)_2(H_2O)_4$	trans	-731.85
$Ni(Cl)_2(MeOH)_2Et_3N$	square-pyramidal, MeOH-axial	-728.36
$Ni(Cl)_2(Et_3N)_2$	tetrahedral	-718.08

B. Isodesmic equations:

The following isodesmic equations are helpful in understanding the energetics for the ligand exchange processes.

(i) $Ni(Cl)_2(H_2O)_4 + 2MeOH \longrightarrow Ni(Cl)_2(MeOH)_2(H_2O)_2 + 2H_2O$

(ii) $Ni(Cl)_2(H_2O)_4 + 4MeOH \longrightarrow Ni(Cl)_2(MeOH)_4 + 4H_2O$

(iii) $Ni(Cl)_2(MeOH)_4 + 2MeO^- \longrightarrow Ni(OMe)_2(MeOH)_4 + 2Cl^-$

(iv) $Ni(Cl)_2(H_2O)_2(MeOH)_2 + 2Et_3N \longrightarrow Ni(Cl)_2(H_2O)_2(Et_3N)_2 + 2MeOH$

(v) $Ni(Cl)_2(MeOH)_4 + Et_3N \longrightarrow Ni(Cl)_2(MeOH)_2Et_3N + 2MeOH$

(vi) $Ni(Cl)_2(MeOH)_4 + 4Et_3N \longrightarrow Ni(OMe)_2(Et_3N)_2 + 2MeOH + 2Et_3HN^+ + 2Cl^-$

(vii) $Ni(Cl)_2(MeOH)_4 + 2Et_3N \longrightarrow Ni(Cl)_2(Et_3N)_2 + 4MeOH$

(viii) $Ni(Cl)_2(MeOH)_4 + 3Et_3N \longrightarrow Ni(Cl)(OMe)(Et_3N)_2 + 3MeOH + Et_3HN^+ + Cl^-$

Scheme I: Plausible isodesmic reactions of $Ni(Cl)_2(H_2O)_4$ in solution phase

Solvation of $NiCl_2.6H_2O$ in methanolic solution and replacement of Cl^- by OMe^-:

The ΔE_{reac} for this two types of reactions are given in table 2 (equation i, ii and iii). The negative ΔE_{reac} shows that the replacement of H_2O by MeOH is thermodynamically favorable.

Table 2: Conversion energies

Conversion	**Isomers**		**ΔE_{reac}(kcal/mol)**
	Substrate complex	Product complex	
i	cis-$Ni(Cl)_2(H_2O)_4$	cis (all)-$Ni(Cl)_2(MeOH)_2(H_2O)_2$	-3.06
		cis-MeOH,cis-Cl,trans-H_2O - $Ni(Cl)_2(MeOH)_2(H_2O)_2$	-2.84
	trans-$Ni(Cl)_2(H_2O)_4$	trans(all)-$Ni(Cl)_2(MeOH)_2(H_2O)_2$	-9.12
		trans-Cl,cis-MeOH,cis-H_2O- $Ni(Cl)_2(MeOH)_2(H_2O)_2$	-6.73
ii	cis- $Ni(Cl)_2(H_2O)_4$	cis-$Ni(Cl)_2(MeOH)_4$	-7.94
	trans- $Ni(Cl)_2(H_2O)_4$	trans-$Ni(Cl)_2(MeOH)_4$	-15.45
iii	cis- $Ni(Cl)_2(MeOH)_4$	cis-$Ni(OMe)_2(MeOH)_4$	-54.33
	trans-$Ni(Cl)_2(MeOH)_4$	trans-$Ni(OMe)_2(MeOH)_4$	-46.26
iv	trans- $Ni(Cl)_2(H_2O)_2(MeOH)_2$	trans-$Ni(Cl)_2(H_2O)_2(Et_3N)_2$	-3.88[I]

I optimized with BP86 method

The exchange of Cl^- by MeO^- is thermodynamically favorable (equations iii, table 2) as seen from high reaction energies.

Exchange of MeOH by Et_3N:

There are many possible ways for replacement of MeOH by Et_3N. Most of the cases, two Et_3N coordination to Ni(II) with other ligands together in a hexacoordinated geometry is highly unlikely because of the large size of the Et_3N. The geometries that we have calculated are given below.

(a) Hexacoordinated geometry: We found a energetically favorable reaction with two Et_3N ligands in the resuling complex. In this geometry the two bulky Et_3N are trans to each other (Figure XII). The reaction energy is not highly negative (equation iv, table 2). The negative energy of formation of $Ni(Cl)_2(H_2O)_2(MeOH)_2$ indicates its presence in methanolic solution. Then Et_3N substituted the two MeOH which are trans to each other (although, this geometry was not found to be stable with B3LYP method, it has an existence when we used BP86 method).

(b) Pentacoordinated geometry: There may exist many possible species when the hexacoordinated Ni(II) complex convert to a pentacoordinated complex and some of the energies of conversion which we have calculated is given in table 3, and in scheme I (equation v). The same geometry in which two MeO^- is coordinated to Ni(II) instead of two Cl^- in the petacoordinated complex was not found. The geometry of $Ni(Cl)_2(MeOH)_2Et_3N$ is distorted square planer (Figure XIII). In this geometry the basal plane is distorted from its ideal structure.

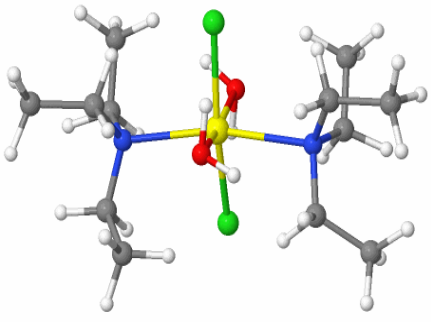

Figure XII: structure of $Ni(Cl)_2(H_2O)_2(Et_3N)_2$ optimized by BP86 method

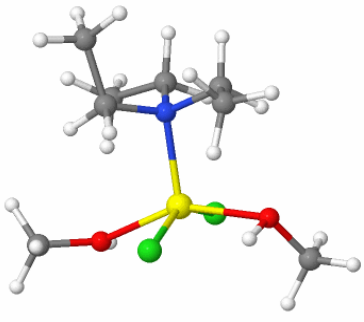

Figure XIII: Structure of $Ni(Cl)_2(MeOH)_2Et_3N$ with Et_3N in axial position

Table 3: energy of formation for pentacoordinated complexes from hexacoordinated complexes

Conversion	**Isomers**		**ΔE_{reac}(kcal/mol)**	**ΔE_{reac}(kcal/mol)**
v	$Ni(Cl)_2(MeOH)_4$	$Ni(Cl)_2(MeOH)_2Et_3N$ (distorted square pyramidal)		
	Cis	MeOH-axial	16.16	-13.04
		Et_3N-axial	12.85	-7.61
	Trans	MeOH-axial	15.38	-18.94
		Et_3N-axial	12.06	-13.51

(c) Tetracoordinated geometry: We calculated the energy for a few conversion from hexacoordinated complex to tetracoordinated complexes (scheme I, equation vi–viii). We also considered both tetrahedral and square planer geometry for this tetracoordinated complexes. $Ni(OMe)_2(Et_3N)_2$ (Figure XIV) and $Ni(Cl)_2(Et_3N)_2$ is found to be tetrahedral but $Ni(Cl)(OMe)(Et_3N)_2$ is distorted. This conversions are seems to be highly unfavorable (Table 4) in terms of thermodynamic stability.

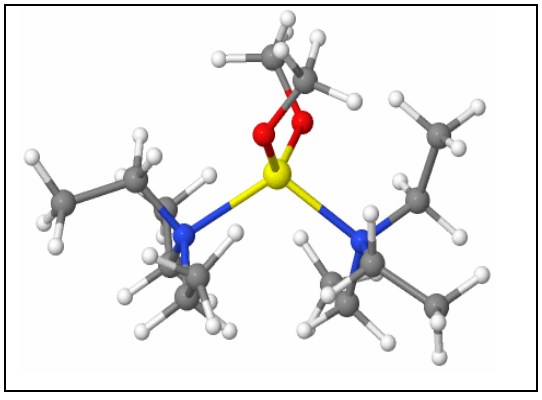

Figure XIV: Structure of $Ni(OMe)_2(Et_3N)_2$

Table 4: energy of formation for tetracoordinated complexes from hexacoordinated (both cis and trans) complex

Conversion	**Isomers**		**ΔE_{reac}(kcal/mol)**
	Substrate complex $Ni(Cl)_2(MeOH)_4$	Product complex	
vi	cis	$Ni(OMe)_2(Et_3N)_2$	66.39
	trans		72.29
vii	cis	$Ni(Cl)_2(Et_3N)_2$	23.32
	trans		29.22
viii	cis	$Ni(Cl)(OMe)(Et_3N)_2$	44.46
	trans		50.36

The coordinates and final single point energies (hartree unit) of the optimized geometries (B3LYP/TZVP) are given below:

(i) cis-$Ni(OMe)_2(MeOH)_4$

35
Energy = -2201.46112724460

C	-1.0350968	1.2628908	-2.8993573
O	-0.3110955	0.1839706	-2.3068333
Ni	-0.1474570	-0.0277817	-0.1082086
O	-0.0812366	2.1124270	0.0682524
C	-0.4322186	2.7282069	1.3096869
O	-0.2224071	-2.0816728	-0.6768360
C	0.5268660	-3.0201146	0.1143852
O	-0.0849572	-0.4936321	1.7859268
C	1.0331376	-0.3139238	2.5905147
O	1.6696430	0.4781268	-0.7860750
C	2.8316711	-0.2717351	-0.6053569
O	-2.2153549	-0.0106236	0.5923093
C	-3.1260146	-1.0578335	0.2637343
H	0.6415038	0.4307702	-2.1349147
H	0.0100078	-2.1395715	-1.6117638
H	0.8895941	2.0212027	-0.0461753
H	-1.7506093	-0.2083604	1.4454960
H	-3.5082571	-0.8556376	-0.7367042
H	-2.6272059	-2.0294456	0.2576061
H	-3.9644109	-1.0749879	0.9659834
H	-1.5181189	2.7004193	1.3739446
H	-0.0176528	2.1766010	2.1542377
H	-0.0919862	3.7666001	1.3304475
H	-2.0884951	0.9837389	-2.9071481

H	-0.9168654	2.1773367	-2.3147606
H	-0.7048839	1.4311510	-3.9284778
H	0.2130336	-4.0412294	-0.1128851
H	1.5989504	-2.9072570	-0.0560625
H	0.3010773	-2.7656111	1.1465910
H	3.7211149	0.3006317	-0.9050389
H	2.9720704	-0.5699955	0.4437415
H	2.8317314	-1.1968267	-1.2071358
H	0.7492892	-0.1670831	3.6437917
H	1.7149432	-1.1822753	2.5606980
H	1.6381346	0.5590625	2.2922896

(ii) trans-Ni(OMe)$_2$(MeOH)$_4$

35
Energy = -2201.45766593442

O	0.4949815	-0.3753755	2.2202293
Ni	-0.1599251	-0.0012691	0.2087217
O	-0.9392517	-1.7861373	0.0553487
O	2.0120545	-0.2236503	-0.0985033
O	-0.3239190	0.7130313	-1.8724576
O	-2.1965923	0.1428012	0.9417062
O	0.5862257	1.8556684	0.1314026
C	0.3138104	2.7985136	1.1289504
C	-1.4802554	0.9354251	-2.6686813
H	-0.0155287	1.5456849	-1.4205356
H	-2.1803303	-0.7960042	0.5920899
C	-3.2890340	0.8972108	0.4359837
C	-0.7441406	-2.5508116	-1.0923873
H	1.3471636	-0.7892774	2.0267597
C	-0.3102085	-1.2687361	3.0122274
C	2.5630684	-0.6609995	-1.3432134
H	1.9370963	0.7665307	-0.0581560
H	-1.4236134	-3.4156465	-1.1088026
H	-0.9131051	-1.9844325	-2.0236382
H	0.2824600	-2.9481478	-1.1531119
H	3.6058520	-0.3450936	-1.4329769
H	2.5171950	-1.7487632	-1.3518114
H	1.9800519	-0.2747235	-2.1815565
H	-1.1986430	1.2978968	-3.6618100
H	-2.0030762	-0.0150044	-2.7756826
H	-2.1555302	1.6598176	-2.2055116
H	-4.1855697	0.7249208	1.0389111
H	-3.0241871	1.9535044	0.4940088
H	-3.5090233	0.6445669	-0.6046717
H	0.1997783	-1.5040144	3.9490035
H	-1.2344049	-0.7355699	3.2182109
H	-0.5389011	-2.1704060	2.4433705
H	0.8925837	3.7185675	0.9694159
H	-0.7511721	3.0792288	1.1484552
H	0.5619821	2.4120376	2.1268706

(iii) tetrahedral $Ni(OMe)_2(NEt_3)_2$

55
Energy = -2323.25594766006

C	0.2564078	-3.3236646	0.8221307
C	-0.1718065	-3.0425440	-0.6081951
N	-1.0705845	-1.8656374	-0.7688655
C	-2.2744543	-1.9279482	0.1074172
C	-3.1472556	-3.1775756	-0.0001734
Ni	-0.0576680	-0.0858647	-0.0662594
N	-1.0821593	1.8023601	-0.8827381
C	-0.7069366	1.9562481	-2.3121543
C	0.7879348	2.0428201	-2.5855211
O	-0.5331687	0.3669198	1.6796967
O	1.6169267	-0.6859014	-0.6348462
C	-0.4899763	2.8591465	-0.0184182
C	-0.8930564	4.2985996	-0.3344608
C	-2.5658489	1.7765470	-0.8073035
C	-3.1417153	1.7022512	0.5993622
C	-1.4751066	-1.7346520	-2.1924270
C	-0.3114133	-1.5830805	-3.1662410
H	-0.6558599	-3.9256307	-1.0460270
H	0.7231358	-2.8192781	-1.1813748
H	-2.0854749	-2.5962767	-2.4899964
H	-2.1198838	-0.8571097	-2.2497126
H	-2.8690444	-1.0447866	-0.1234927
H	-1.9345124	-1.7928585	1.1318154
H	0.9499514	-4.1666003	0.8198326
H	0.7778623	-2.4621925	1.2339417
H	-0.5744229	-3.5813198	1.4799432
H	-3.9913458	-3.0755046	0.6849028
H	-3.5546055	-3.3218717	-1.0017491
H	-2.6057036	-4.0818799	0.2794939
H	-0.6872278	-1.2094286	-4.1205809
H	0.4385041	-0.8933846	-2.7797032
H	0.1848439	-2.5342806	-3.3578602
H	-1.1159421	1.0900476	-2.8335997
H	-1.2103361	2.8364469	-2.7352919
H	-0.7378553	2.5929335	1.0054204
H	0.5927456	2.7537802	-0.0867069
H	-2.8864896	0.9044275	-1.3811258
H	-2.9790890	2.6491069	-1.3330674
H	0.9531123	2.0042566	-3.6638549
H	1.2192310	2.9754356	-2.2210980
H	1.3226980	1.2080862	-2.1310292
H	-0.3958728	4.9683518	0.3697950
H	-0.5998357	4.6033329	-1.3408061
H	-1.9681274	4.4574549	-0.2327450
H	-4.2035679	1.4548862	0.5368371
H	-2.6206767	0.9539847	1.1958405

H	-3.0578775	2.6561674	1.1219154
C	-0.0138996	-0.3003214	2.7853546
H	-0.0661239	0.3384692	3.6792546
H	-0.5673181	-1.2261567	3.0215547
H	1.0424805	-0.5873026	2.6551432
C	2.7568667	-0.0510680	-0.1391496
H	3.6292558	-0.2623658	-0.7745736
H	2.6556567	1.0476445	-0.0864232
H	3.0041475	-0.3915064	0.8788261

(iv) trans-Ni(Cl)$_2$(MeOH)$_4$

27
Energy = -2891.65454166682

O	2.0299905	-0.1608667	-0.6706809
Ni	-0.0000094	0.0000070	-0.0000252
O	0.3064231	2.0694138	0.4778885
O	-0.3064395	-2.0694018	-0.4779382
Cl	0.5109181	-0.3631095	2.2786535
Cl	-0.5109379	0.3631227	-2.2787037
O	-2.0300111	0.1608824	0.6706304
H	1.8736475	-0.1865767	-1.6282695
C	-2.7942757	1.3045302	0.2464714
H	-0.7239809	-1.9550852	-1.3470433
C	2.7942630	-1.3045073	-0.2465171
C	-1.1303341	-2.8727891	0.3851700
C	1.1303139	2.8728040	-0.3852205
H	-1.8736649	0.1865891	1.6282186
H	3.8022742	-1.2543104	-0.6627980
H	2.8292704	-1.2568351	0.8383599
H	2.2989426	-2.2289528	-0.5462440
H	-1.1622534	-3.9011050	0.0196653
H	-0.6650634	-2.8352446	1.3666253
H	-2.1372337	-2.4579396	0.4506021
H	0.7239655	1.9550980	1.3469931
H	1.1622301	3.9011199	-0.0197154
H	2.1372148	2.4579578	-0.4506541
H	0.6650419	2.8352583	-1.3666752
H	-3.8022889	1.2543364	0.6627478
H	-2.2989514	2.2289710	0.5462062
H	-2.8292791	1.2568652	-0.8384061

(v) tetrahedral-NiCl(OMe)(NEt$_3$)$_2$

51
Energy = -2668.34826690666

Ni	-0.4029527	-0.0962738	0.0640255
Cl	-1.7075270	-0.0789827	1.9358335
O	1.3696658	-0.4662202	-0.3653663
N	-1.0256418	1.8133828	-0.8200228
N	-1.1260831	-1.9595213	-0.8098074

C	2.3739942	0.2519598	0.2873732
H	2.7887431	1.0532361	-0.3483110
H	2.0333138	0.7288205	1.2229086
H	3.2103532	-0.4087986	0.5550875
C	-0.7606418	1.8142591	-2.2886513
C	-0.1924117	2.8739776	-0.1733331
C	-2.4869116	2.0095748	-0.5772936
C	-1.2295599	-2.9365649	0.3202338
C	-0.2184174	-2.5219071	-1.8473113
C	-2.4877562	-1.6423620	-1.3138932
H	-1.5820436	-3.8941090	-0.0796963
C	0.0572954	-3.1653709	1.1005805
H	-1.9866180	-2.5484638	0.9978615
C	-0.1785862	-1.7616679	-3.1604037
H	0.7776659	-2.5021742	-1.4139065
H	-0.4951490	-3.5676179	-2.0324942
H	-2.3783919	-0.8590836	-2.0634544
C	-3.2996755	-2.7949878	-1.9047205
H	-3.0215169	-1.2000447	-0.4718644
H	-1.1874173	2.7204982	-2.7311235
C	0.7069933	1.7201440	-2.6879072
H	-1.3115636	0.9685834	-2.7012669
H	-2.6583973	1.8189140	0.4778586
C	-3.0880202	3.3555733	-0.9813216
H	-2.9938948	1.2070718	-1.1138515
C	-0.4683924	3.1327541	1.3001350
H	0.8440616	2.5615919	-0.2829722
H	-0.3050546	3.8052084	-0.7427392
H	0.7661135	1.5340304	-3.7620709
H	1.2432082	2.6484750	-2.4916965
H	1.2072968	0.9058514	-2.1626484
H	0.2535609	3.8694212	1.6584634
H	-1.4666923	3.5317915	1.4782544
H	-0.3673768	2.2267137	1.8944601
H	-4.1471120	3.3506081	-0.7161238
H	-2.6262603	4.1912088	-0.4539168
H	-3.0217826	3.5519329	-2.0519384
H	-4.2460978	-2.4029009	-2.2825322
H	-2.7857515	-3.2772024	-2.7378265
H	-3.5340621	-3.5563224	-1.1611923
H	-0.1531869	-3.8706683	1.9069794
H	0.8533658	-3.5849509	0.4863693
H	0.4208854	-2.2417273	1.5469375
H	0.5773372	-2.2148009	-3.8041710
H	-1.1263116	-1.7846948	-3.7005884
H	0.1127709	-0.7295953	-2.9944464

(vi) cis-$Ni(Cl)_2(MeOH)_4$

27
Energy = -2891.64513532719

Ni	0.1448209	0.1034582	0.0813880
Cl	0.2991696	0.0792885	2.4070461
Cl	2.3408321	0.1810102	-0.7959841
O	-0.3395011	0.0191127	-2.0546444
O	-1.9754384	0.2274612	0.5275917
O	0.2141460	2.2334112	-0.0873986
O	0.0548505	-2.0129817	-0.1285635
H	0.5929452	0.1780546	-2.3007643
C	-1.1860746	1.0262869	-2.6287417
C	1.0146262	-2.7712803	0.6454663
H	0.2351169	-2.1449977	-1.0685711
H	1.1798284	2.3290724	-0.1103042
C	-0.3610155	3.0891478	0.9164137
H	-1.7731841	0.2377702	1.4853969
C	-2.8152472	-0.8983947	0.2326875
H	-2.8424666	-1.0021200	-0.8503663
H	-2.4032151	-1.8126794	0.6599516
H	-3.8259461	-0.7219465	0.6069718
H	-1.4331382	2.9076371	0.8914535
H	0.0233970	2.8344390	1.9036060
H	-0.1598644	4.1342720	0.6730083
H	-2.1687944	0.9081106	-2.1776116
H	-0.8110874	2.0223858	-2.3935937
H	-1.2592503	0.8877329	-3.7093710
H	0.8986177	-3.8348844	0.4291287
H	2.0255581	-2.4308787	0.4219544
H	0.7892894	-2.5644986	1.6867344

(vii) alltrans-Ni(Cl)$_2$(H$_2$O)$_2$(MeOH)$_2$

21
Energy = -2813.07874302979

O	2.3081755	0.1824460	-0.7636297
Ni	0.1877001	-0.0008923	-0.4509268
O	-0.0553174	2.1256908	-0.4964414
O	0.4298639	-2.1277893	-0.4055036
Cl	0.5002138	-0.1309671	1.8671498
Cl	-0.1250746	0.1289597	-2.7694164
O	-1.9335192	-0.1822583	-0.1404753
H	2.4502228	-0.2604619	-1.6126071
H	-2.3445990	0.3485066	-0.8366835
H	0.0072779	2.2584637	-1.4562795
C	-0.5397111	-2.9417406	-1.0916411
H	2.7222650	-0.3515522	-0.0717665
H	0.3698207	-2.2586055	0.5548205
C	0.9085163	2.9420559	0.1948199
H	-2.0779062	0.2654836	0.7055023
H	0.6437007	3.9964294	0.0943866
H	0.8686100	2.6384916	1.2372503
H	1.9123967	2.7599099	-0.1911314
H	-0.2790347	-3.9970004	-0.9897395

H	-1.5414111	-2.7544259	-0.7025755
H	-0.5021391	-2.6407565	-2.1349092

(viii) trans-Cl,cis-H_2O,cis-MeOH-Ni$(Cl)_2(H_2O)_2(MeOH)_2$

21
Energy = -2813.07493861761

O	2.1502133	-0.0263596	-0.7665774
Ni	0.0883792	-0.0192344	-0.1144314
O	-0.0915535	2.0117041	-0.6246880
O	0.3542601	-2.1574109	0.2515276
Cl	0.7439991	0.2601453	2.1199652
Cl	-0.5252307	-0.5969221	-2.3000160
O	-1.9128361	0.0571511	0.6177908
H	2.1164340	-0.6340958	-1.5203922
H	-1.7771583	0.1843865	1.5691887
H	-0.2528606	1.9717698	-1.5789531
H	-0.2905610	-2.6497743	-0.2730263
H	2.6313459	-0.4646849	-0.0512561
H	0.1944885	-2.3078665	1.1934975
C	1.0040204	2.8949463	-0.3256834
C	-2.8817424	-0.9616546	0.3514979
H	-3.8780707	-0.6245658	0.6444399
H	-2.8478374	-1.1361622	-0.7213325
H	-2.6431903	-1.8899272	0.8808142
H	0.7257768	3.9241922	-0.5601766
H	1.1895266	2.7886672	0.7400847
H	1.8996489	2.6030209	-0.8757992

(ix) allcis-Ni$(Cl)_2(H_2O)_2(MeOH)_2$

21
Energy = -2813.07165846012

O	-0.2223956	0.0155554	0.6259318
Ni	0.0599210	-0.0020664	2.7849309
O	-0.2167338	-2.1345130	2.5652516
O	-2.0319424	0.0334394	3.0863289
O	2.2191545	-0.1724764	2.6447213
Cl	0.2478792	-0.2610311	5.0942882
Cl	0.4076727	2.3017317	2.4023226
H	0.4068881	-0.5445675	0.1562402
H	-1.0186869	-2.2627327	3.0896685
C	-2.8424851	0.9376392	2.3078227
H	2.3758544	-0.3076078	3.5948806
H	2.3600547	0.7819587	2.5057018
H	0.0616035	0.9432979	0.5161653
C	0.8170600	-3.0050665	3.0650317
H	-2.0367690	0.2885311	4.0229637
H	0.5237338	-4.0484879	2.9352669
H	1.7037305	-2.7980080	2.4704942
H	1.0203664	-2.7872014	4.1142978

H	-3.8793835	0.8888078	2.6441633
H	-2.4525363	1.9527824	2.3812544
H	-2.7699337	0.5971978	1.2783794

(x) cis-MeOH,cis-Cl,trans-H_2O-Ni$(Cl)_2(H_2O)_2(MeOH)_2$

21
Energy = - 2813.07131479063

O	0.3166563	-0.6480754	0.6108008
Ni	0.1712755	-0.0790356	2.6886242
O	0.0121975	-2.2478287	2.8054082
O	-1.9593858	0.2133622	2.7039971
O	2.3267113	-0.1946737	2.7950078
Cl	0.0891575	-0.2899060	5.0441993
Cl	0.4033924	2.1901343	2.2578298
H	0.9417745	-1.3838618	0.6318379
C	-1.2413828	-2.8392770	2.4216541
H	-1.9591137	1.1447972	2.4254721
H	2.4383915	-0.3399124	3.7483417
H	2.4697865	0.7593545	2.6657028
C	0.6687900	0.2574520	-0.4529287
H	0.0917072	-2.2624384	3.7773188
H	-2.0705083	0.2413094	3.6693982
H	0.5397107	-0.2388457	-1.4169609
H	0.0002096	1.1077985	-0.3679348
H	1.6935878	0.6138097	-0.3388433
H	-1.1947038	-3.9239818	2.5364880
H	-2.0617800	-2.4320503	3.0137946
H	-1.4032169	-2.5810094	1.3780274

(xi) dist-sq pyramidal,NEt_3-axial-Ni$(Cl)_2(MeOH)_2(NEt_3)$

37
Energy = -2952.54868602430

C	-2.3253685	2.1091067	0.3665967
O	-2.0106518	0.9149356	-0.3702882
H	-1.9671025	2.0409479	1.3944457
H	-1.8041450	2.9257225	-0.1235170
H	-3.4038874	2.2798225	0.3458670
H	-2.4007429	0.1361724	0.0603095
Ni	0.0003026	0.1097885	-0.5335607
Cl	0.9661291	2.0950177	0.1301527
N	0.0972350	0.0198909	-2.6547217
C	0.9563842	1.1337845	-3.1744618
C	2.4469172	1.0286199	-2.8988581
Cl	-1.0110173	-1.8318220	0.2033248
C	-1.2677270	0.2447495	-3.2312697
C	-2.2800930	-0.8680134	-3.0117797
C	0.6373782	-1.3290266	-2.9868169
C	0.7973117	-1.6408908	-4.4724914
H	-1.1614704	0.4290718	-4.3061379

H	-1.6337742	1.1658899	-2.7816156
H	1.5952521	-1.4127868	-2.4787906
H	-0.0201711	-2.0527149	-2.5096048
H	0.7962856	1.2134736	-4.2556892
H	0.5727825	2.0452543	-2.7171761
H	2.9250592	1.9331370	-3.2792778
H	2.6518161	0.9673565	-1.8356037
H	2.9075309	0.1761737	-3.3992191
H	1.1971206	-2.6511321	-4.5788114
H	-0.1516213	-1.6056988	-5.0083031
H	1.4908742	-0.9594407	-4.9672119
H	-3.2623286	-0.5055589	-3.3205826
H	-2.0555447	-1.7542171	-3.6068692
H	-2.3344384	-1.1703827	-1.9695266
O	1.9902238	-0.6853999	-0.1578052
C	2.2454887	-1.8652302	0.6233725
H	3.3227943	-2.0129666	0.7248545
H	1.7713590	-1.7964285	1.6027891
H	1.8002880	-2.6975831	0.0866241
H	2.3323487	0.1049797	0.2922924

(xii) cis-Ni(Cl)$_2$(H$_2$O)$_4$

15
Energy = -2734.50108174741

O	0.0429784	-0.3310164	0.3031676
Ni	0.0145223	-0.2345065	2.4391745
O	-2.1018340	-0.1381867	2.7027542
O	2.1438490	-0.0812856	2.4116123
Cl	0.1287072	-0.5235741	4.7996432
Cl	0.0049855	2.1039827	1.9856015
O	-0.1281163	-2.3683196	2.4945336
H	0.9388905	-0.6020519	0.0477120
H	-1.0474136	-2.5943528	2.2820355
H	-2.2369596	0.7971842	2.4621250
H	2.3141565	-0.2671398	3.3537515
H	2.1389844	0.8954552	2.3560779
H	0.0392854	0.6485591	0.2226178
H	-0.0791847	-2.3869299	3.4756317
H	-2.0466001	-0.1297716	3.6794888

(xiii) trans-Ni(Cl)$_2$(H$_2$O)$_4$

15
Energy = -2734.49851258405

O	2.0438250	0.2424279	-0.3053538
Ni	-0.0985056	0.1358692	-0.0502083
O	0.1594380	-2.0247388	-0.1090325
Cl	0.1788336	-0.0709782	2.2499654
Cl	-0.3870621	0.0281349	-2.3642788
O	-2.1967136	0.1682640	0.2287128

O	-0.1064654	2.2627335	-0.1245423
H	2.2000209	-0.2582157	-1.1188149
H	-2.4456751	-0.1920490	1.0899097
H	0.0380514	2.4429873	-1.0655481
H	-0.3617407	-2.3996105	-0.8310591
H	2.3773659	-0.2827158	0.4364809
H	-0.1391502	-2.3828504	0.7381792
H	0.6664715	2.5882790	0.3548099
H	-2.7044072	-0.2574574	-0.4727456

(xiv) dist-sq pyramidal,MeOH-axial-Ni(Cl)$_2$(MeOH)$_2$NEt$_3$

37
Energy = -2952.54002207045

Ni	0.0969121	-0.5961499	0.8661037
Cl	-1.1144316	-0.0054902	2.6867974
Cl	2.0464155	-0.8909014	-0.4056374
N	-0.5899088	-2.6727979	0.6085032
C	-0.6704247	-2.8651709	-0.8698510
C	-1.9165676	-2.8630289	1.2754074
C	0.4847272	-3.5155586	1.1993391
C	0.8153630	-3.1610609	2.6427636
H	0.2113472	-4.5720419	1.1331996
H	1.3684441	-3.3648062	0.5815306
H	-1.9142524	-2.2515885	2.1715826
H	-2.6555513	-2.4165487	0.6079663
C	-2.3350456	-4.2854529	1.6541590
C	-1.0861673	-4.2364774	-1.4028554
H	-1.3622020	-2.1086671	-1.2382177
H	0.3116078	-2.6077366	-1.2602812
H	-0.9525340	-4.2348518	-2.4869305
H	-0.4743047	-5.0452006	-1.0010846
H	-2.1332821	-4.4619438	-1.2038006
H	1.5770172	-3.8488778	3.0147134
H	1.2159947	-2.1488998	2.7299974
H	-0.0518887	-3.2223674	3.2989951
H	-3.3472988	-4.2391020	2.0615401
H	-2.3446809	-4.9829259	0.8194869
H	-1.6967762	-4.7029418	2.4341375
O	-0.9438017	0.2168345	-0.7359503
H	-0.2445065	0.4071844	-1.3782263
C	-1.7188836	1.4072428	-0.4689809
H	-2.4030092	1.1452500	0.3323690
H	-1.0677092	2.2121021	-0.1312247
H	-2.2674820	1.6933192	-1.3677511
O	1.0728062	1.4869981	0.9778364
H	1.8831445	1.1946274	0.5273913
C	1.3940822	2.1505123	2.2075648
H	0.4549009	2.3229764	2.7249753
H	2.0288769	1.5246776	2.8394053
H	1.8944791	3.1007979	2.0038114

(xv) tetrahedral-$Ni(Cl)_2(NEt_3)_2$

47
Energy = -3013.43932009430

Ni	-0.1542847	-0.0250623	-0.0740520
Cl	-0.6563031	0.2111462	2.1213784
Cl	1.9733071	-0.4088206	-0.7035622
N	-1.0868813	1.7301200	-0.9552812
N	-1.2003979	-1.7879399	-0.7170751
C	-1.5316782	-1.7523182	-2.1716146
C	-0.3034096	-2.9564424	-0.4400477
C	-2.4669379	-1.8535537	0.0783858
C	-0.5093820	2.8326664	-0.1245118
C	-2.5830264	1.7219716	-0.9118986
C	-0.7193516	1.8702711	-2.4042338
H	-0.7565134	-3.8528049	-0.8799192
H	0.6260037	-2.7592599	-0.9660609
C	0.0157933	-3.1899641	1.0282320
H	-2.1420096	-2.6262481	-2.4209638
H	-2.1631784	-0.8769846	-2.3222644
C	-0.3408837	-1.7002575	-3.1205241
H	-3.0613628	-0.9912637	-0.2199361
C	-3.3075967	-3.1224085	-0.0532522
H	-2.1960950	-1.6885577	1.1169519
H	0.7397562	-4.0039782	1.0949739
H	0.4573330	-2.3060174	1.4857631
H	-0.8588591	-3.4728147	1.6144966
H	-4.1854806	-3.0171785	0.5870939
H	-3.6645219	-3.2972530	-1.0686738
H	-2.7692118	-4.0108028	0.2774351
H	-0.7034609	-1.4699498	-4.1244727
H	0.3845866	-0.9444563	-2.8249608
H	0.1818745	-2.6545123	-3.1711309
C	0.7391121	2.1631811	-2.7189122
H	-1.0168896	0.9400335	-2.8859585
H	-1.3438726	2.6579527	-2.8406966
C	-0.9304919	4.2511865	-0.5001023
H	-0.7722842	2.6157325	0.9073574
H	0.5743846	2.7316586	-0.1825371
H	-2.8971308	0.8266275	-1.4495442
C	-3.2350627	1.7536182	0.4604436
H	-2.9493613	2.5704884	-1.5012738
H	0.8687003	2.1145363	-3.8020955
H	1.0366228	3.1620065	-2.3999198
H	1.4080685	1.4381342	-2.2615132
H	-0.4252365	4.9511593	0.1674606
H	-0.6570064	4.5156534	-1.5221351
H	-2.0039964	4.4075319	-0.3843184
H	-4.3131083	1.6394163	0.3281314
H	-2.8686832	0.9622760	1.1087546
H	-3.0666869	2.7014827	0.9719591

Conclusion from the theoretical study:

The conversion of $NiCl_2.6H_2O$ to $Ni(Cl)_2(MeOH)_4$ is thermodynamically favored (from complexation energy as well as conversion energy) from $Ni(Cl)_2(H_2O)_2$. This high stabilization energy indicates the presence of $Ni(Cl)_2(MeOH)_4$ in methanolic solution. Thermodynamic stability data indicates the formation of hexacoordinated complex over pentacoordinated or tetracoordinated complexes. The complexation energy data highly supported the presence of $Ni(OMe)_2(Et_3N)_2$ but the conversion energy data shows high positive value which indicates thermodynamic instability. The high reaction energy as well as complexation energy of 'conversion iii' indicates the predominance of $Ni(MeO)_2(MeOH)_4$ over other species. The other reaction energies which are close to zero or negative indicates the presence of many types of complexes in solution. So the gel formation may not be due to the presence of a specific complex but for a mixture of complexes.

References:

1 All calculations were done using Turbomole 6.4 package.[2] Density Functional Theory using B3LYP[3] functionals with def2-TZVP basis set,[4] Empirical Dispersion correction (D3)[5] for incorporating the corrections for weak interactions were used. All the calculations were done at the triplet-state, which was found to be the ground state. Unrestricted formalism was employed.

2 R. Ahlrichs, TURBOMOLE (v. 6.4); Universitat Karlsruhe: Karlsruhe, Germany, 2012.

3 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785. (c) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.

4 A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.

5 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.