ELECTRONIC SUPPLEMENTARY INFORMATION

Role of *para*-substitution in controlling phosphatase activity of dinuclear Ni^{II} complexes of Mannich-base ligands: experimental and DFT studies†

Ria Sanyal,[a,#] Xuepeng Zhang,[b,#] Prateeti Chakraborty,[a] Franz A. Mautner,[c] Cunyuan Zhao,*[,b] and Debasis Das*[,a]

[a]*Department of Chemistry, University of Calcutta, 92 A.P.C. Road, Kolkata 700009, India. Fax: +913323519755; Tel: +913324837031; E-mail: dasdebasis2001@yahoo.com*

[b]*MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-SenUniversity, Guangzhou 510275, P. R. China. E-mail: ceszhcy@mail.sysu.edu.cn.*

[c]*Institutfuer Physikalische und Theoretische Chemie, Technische Universitaet Graz, A-8010 Graz, Austria*

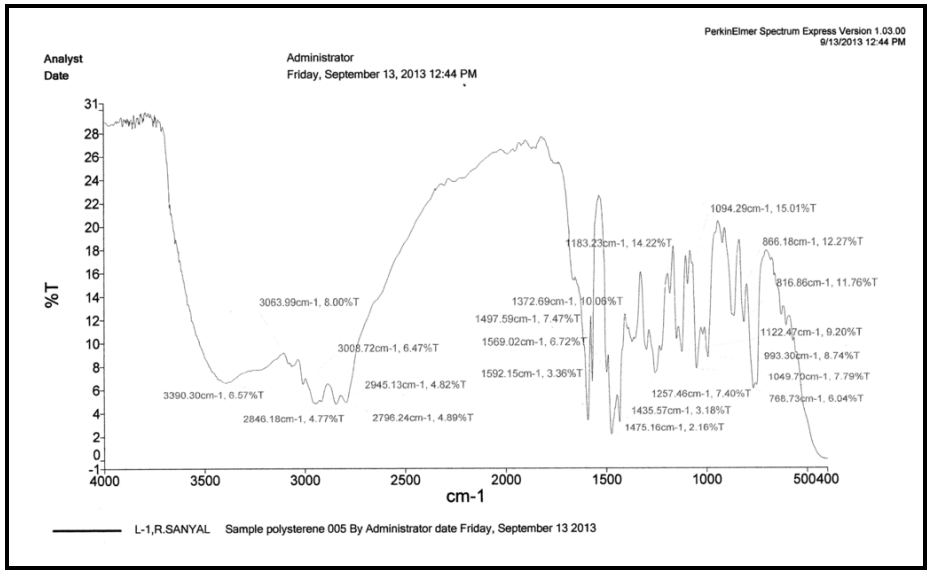

Fig. S1 FTIR spectrum of ligand $\mathbf{HL^1}$ in NaCl plate.

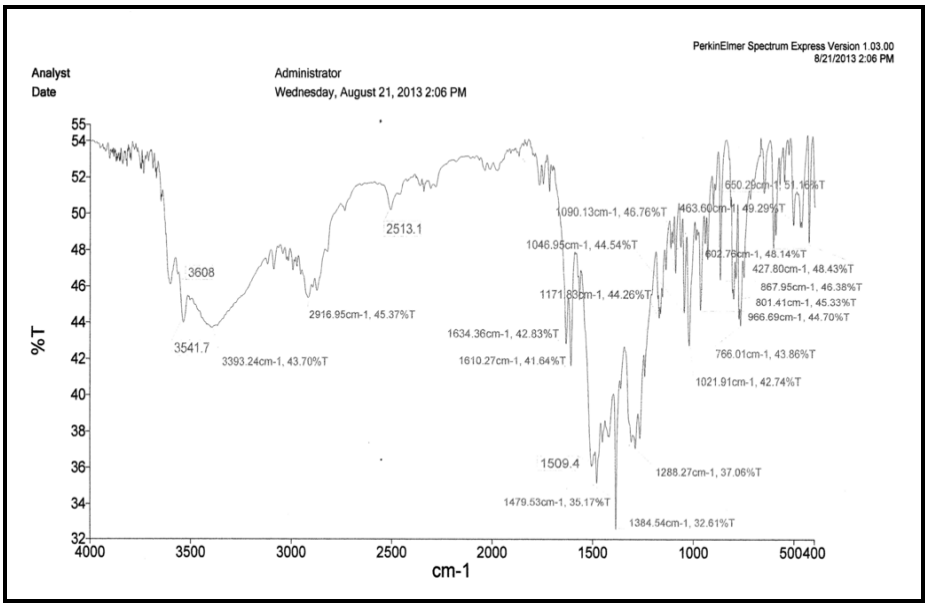

Fig. S2 FTIR spectrum of complex **1** in KBr pellet.

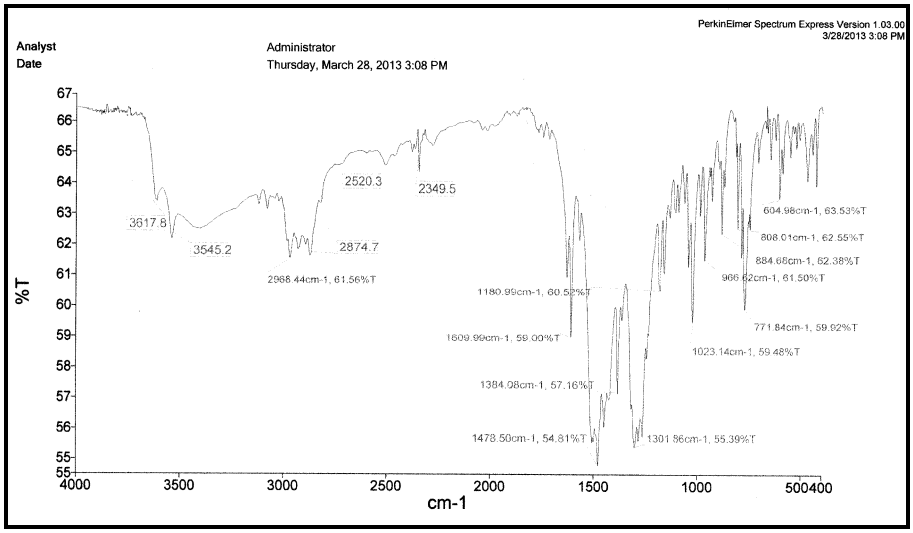

Fig. S3 FTIR spectrum of complex **2** in KBr pellet.

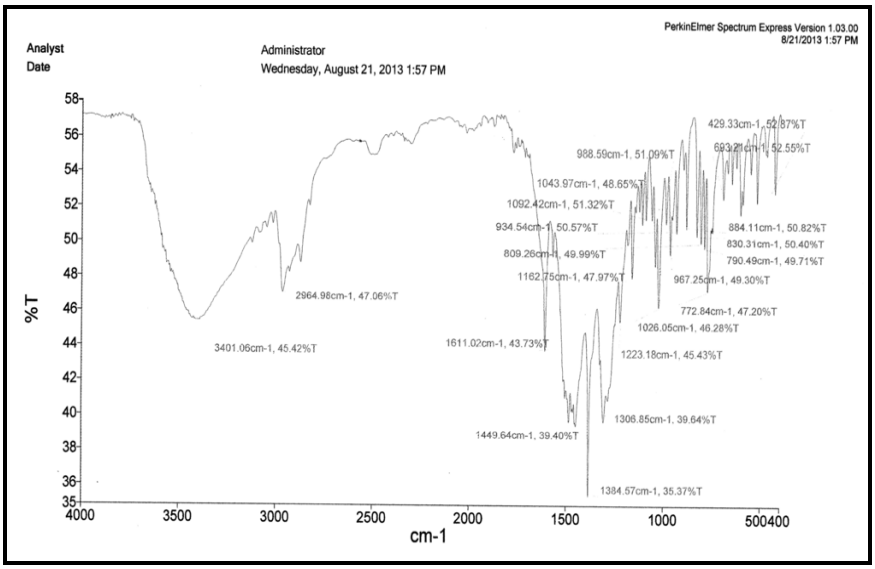

Fig. S4 FTIR spectrum of complex **3** in KBr pellet.

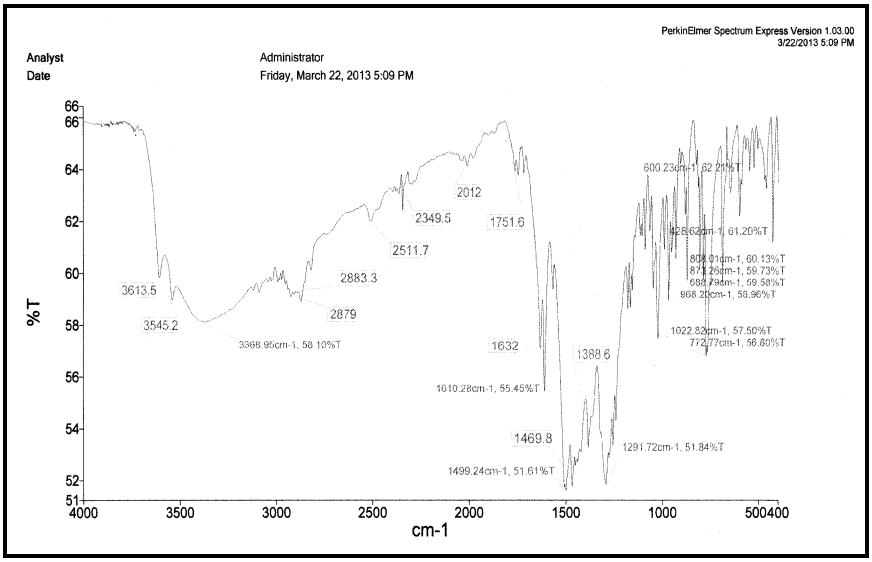

Fig. S5 FTIR spectrum of complex **4** in KBr pellet.

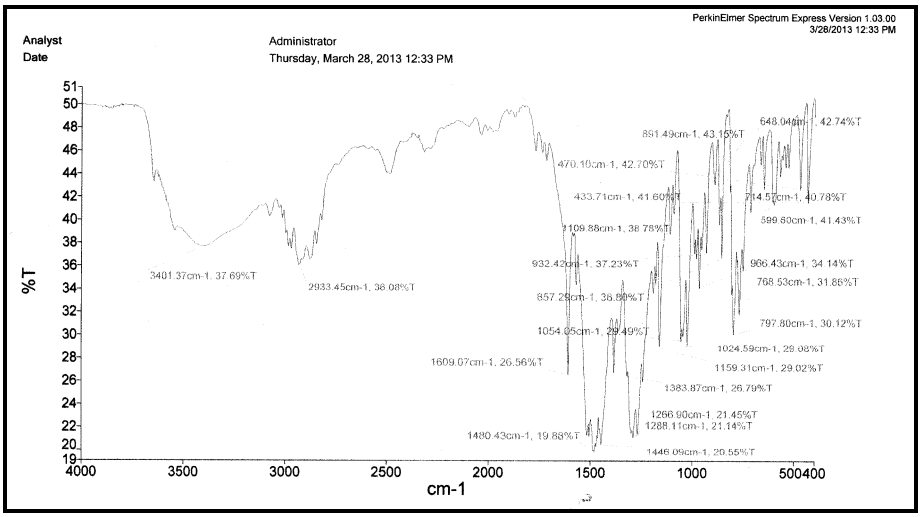

Fig. S6 FTIR spectrum of complex **5** in KBr pellet.

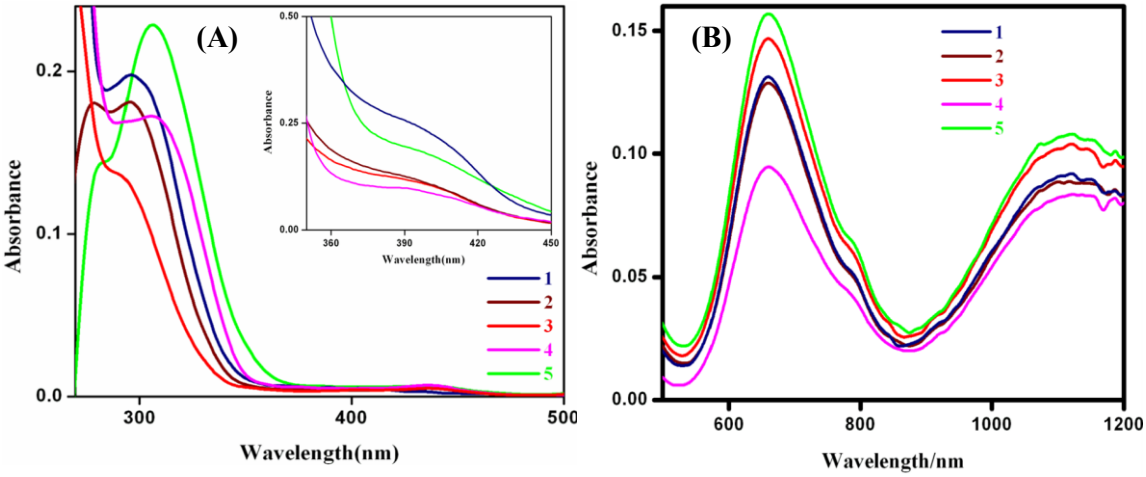

Fig. S7 Electronic spectra of complexes in DMSO of **(A)** 5×10^{-5}(M) where inset shows the same for 1×10^{-3}(M) and **(B)** 5×10^{-3}(M) solution at 298 K.

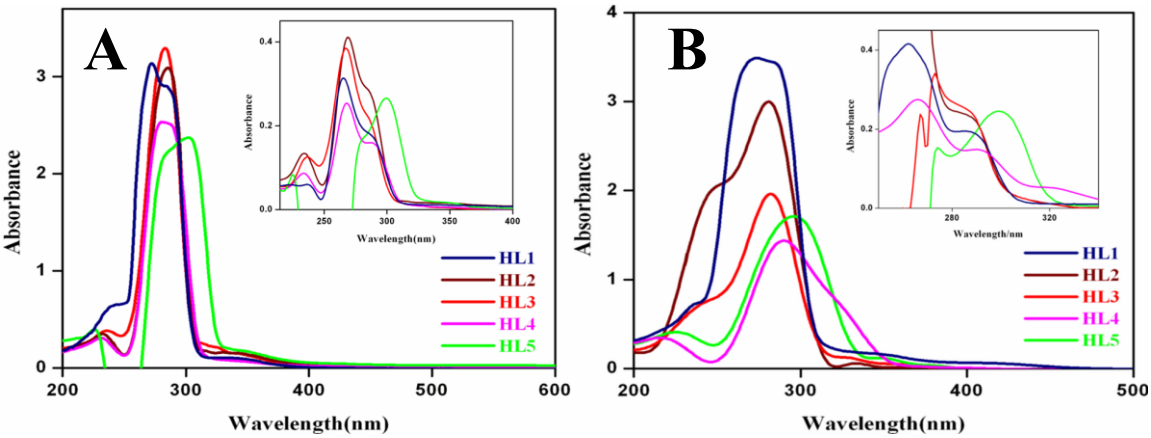

Fig. S8 Electronic spectra of the free ligands of 5×10^{-5} (M) in (A) DMSO and (B) 75% DMSO solution at 298 K. Inset shows the same for 10^{-3} (M) solution.

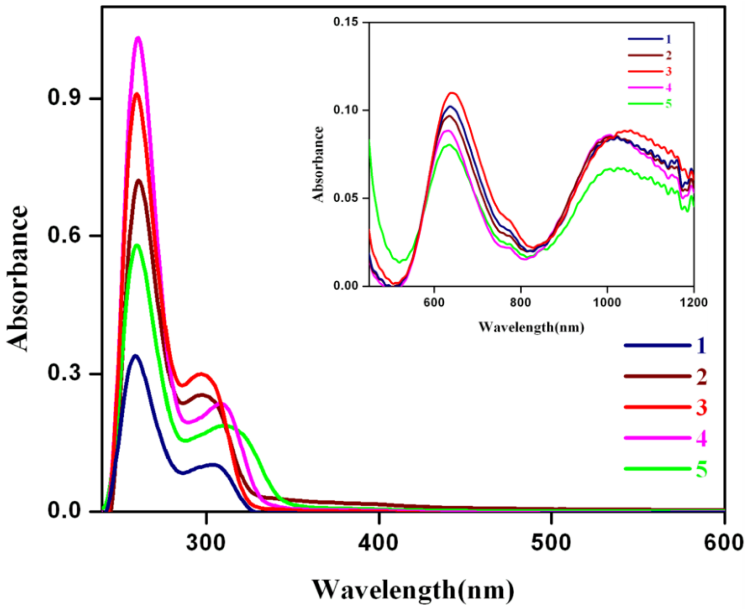

Fig. S9 Electronic spectra of complexes in 75% DMSO of 5×10^{-5}(M) solution at 298 K. Inset shows the same for 5×10^{-3}(M) solution.

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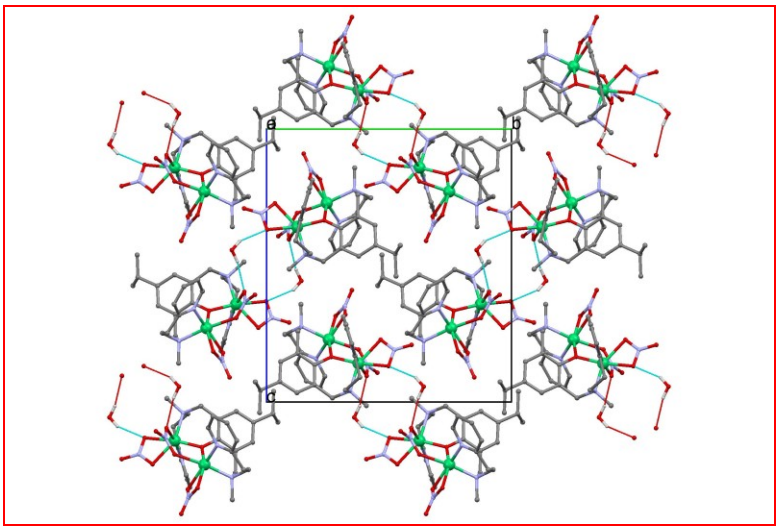


Fig. S10 Packing plot of complex **2**.

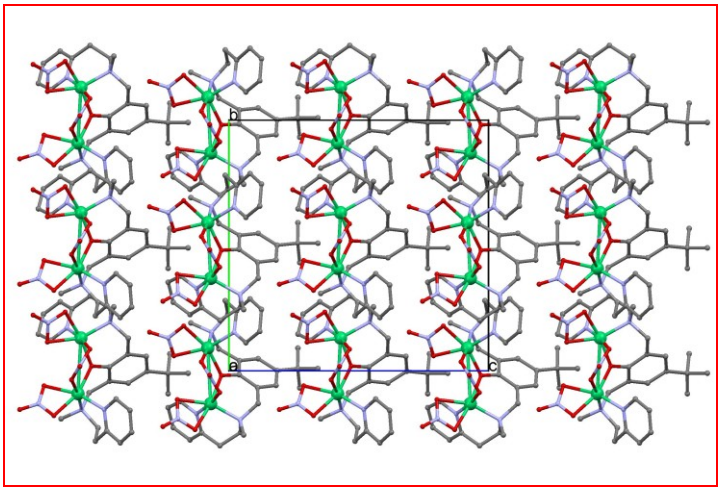


Fig. S11 Packing plot of complex **3**.

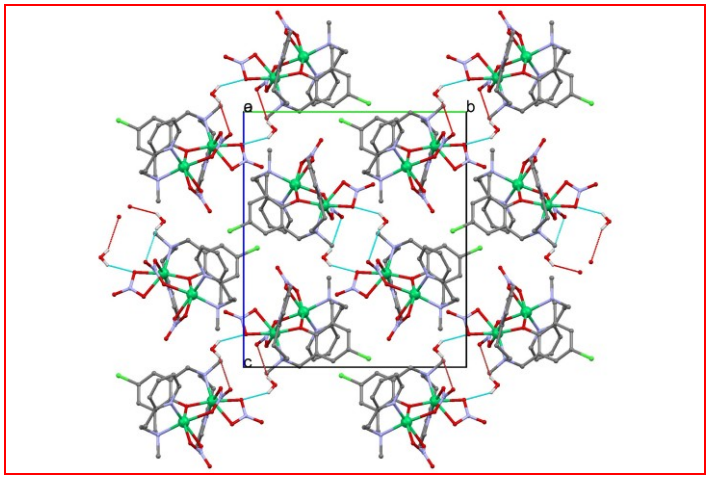
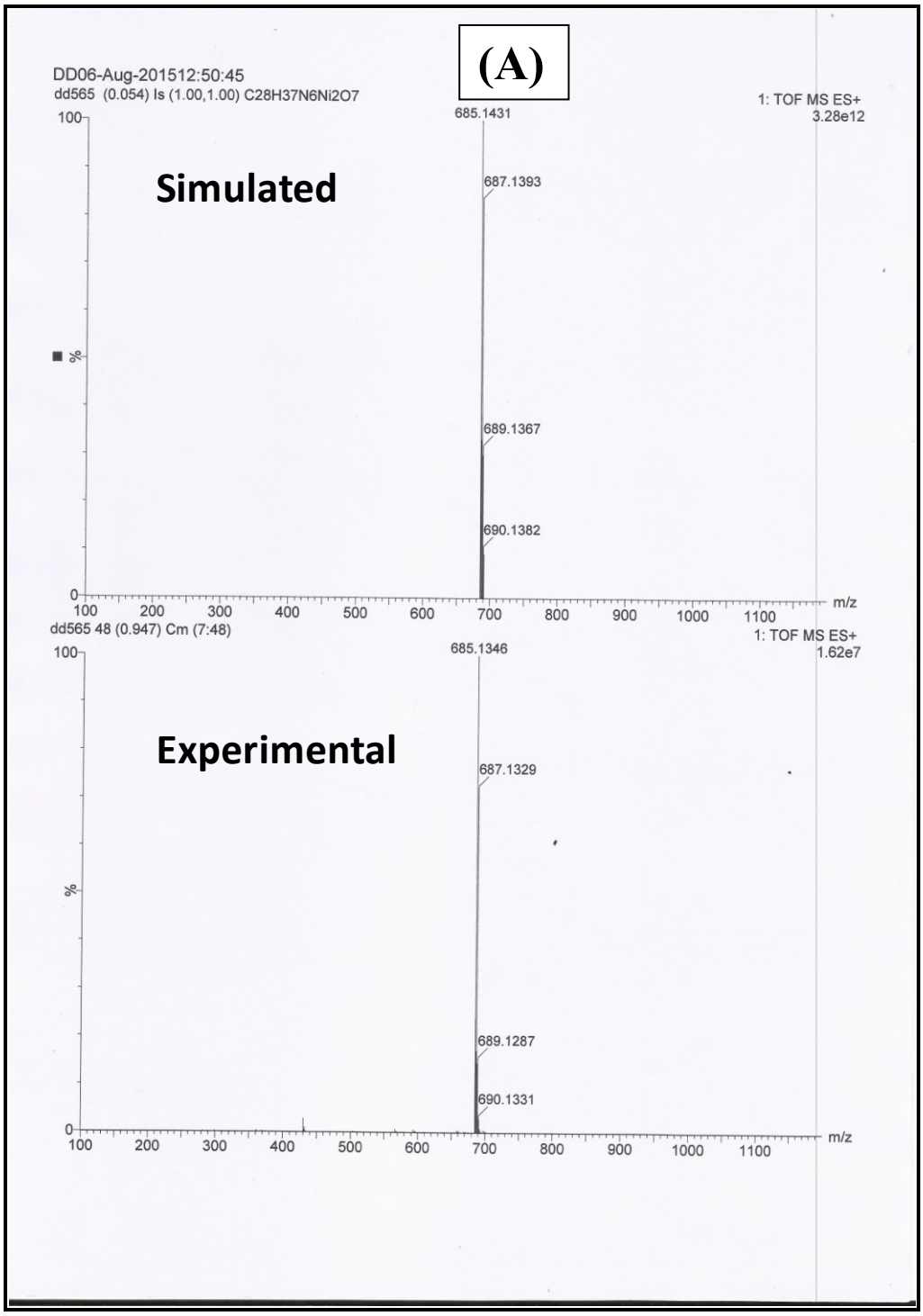


Fig. S12 Packing plot of complex **4**.


(A)
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dd565 (0.054) Is (1.00,1.00) C28H37N6Ni2O7
1: TOF MS ES+
3.28e12
Simulated
685.1431
687.1393
689.1367
690.1382
100
%
0
100 200 300 400 500 600 700 800 900 1000 1100
m/z
dd565 48 (0.947) Cm (7:48)
1: TOF MS ES+
1.62e7
Experimental
685.1346
687.1329
689.1287
690.1331
100
%
0
100 200 300 400 500 600 700 800 900 1000 1100
m/z

(B)

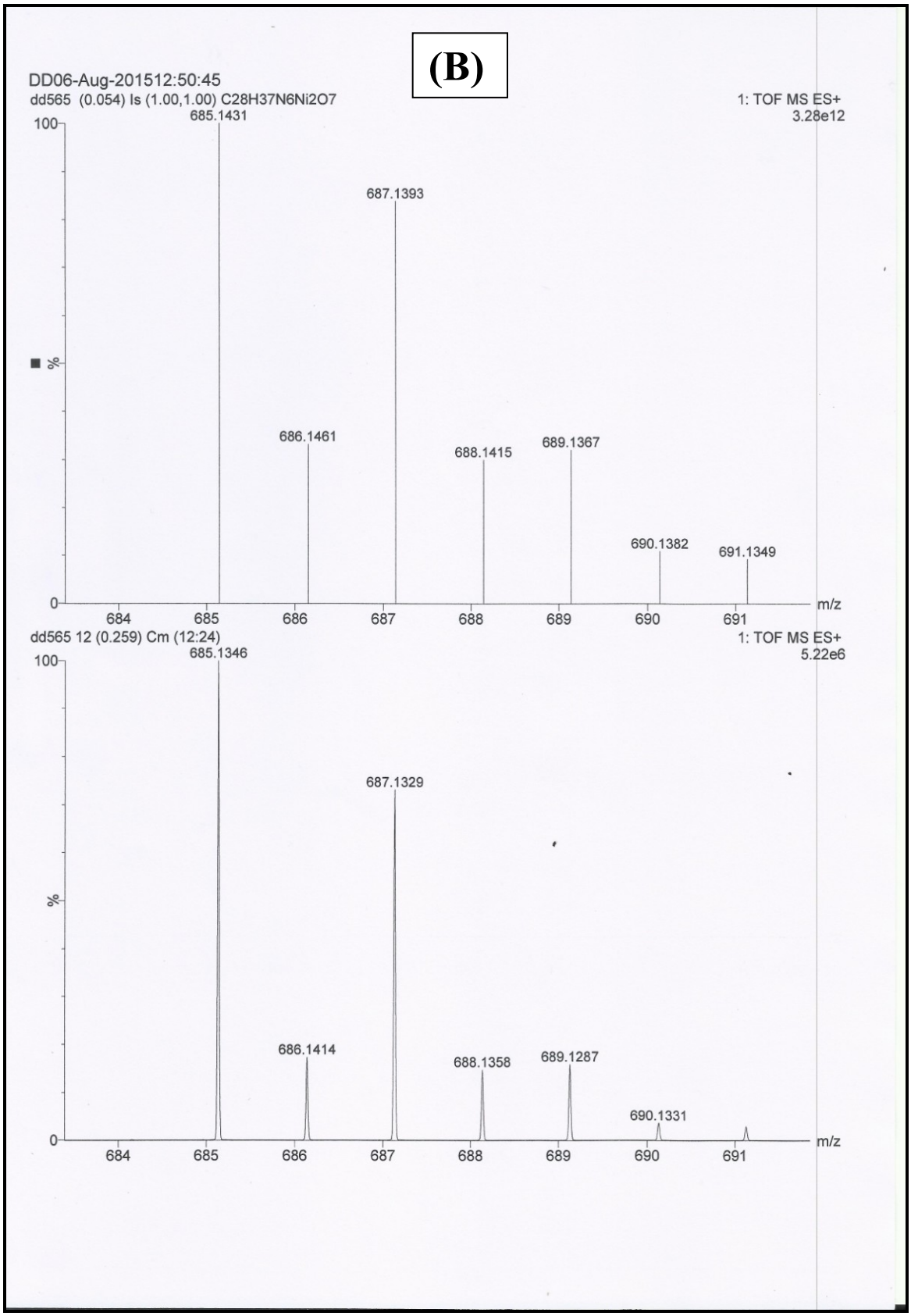
DD06-Aug-201512:50:45
dd565 (0.054) Is (1.00,1.00) C28H37N6Ni2O7
1: TOF MS ES+
3.28e12
685.1431
687.1393
686.1461
688.1415
689.1367
690.1382
691.1349
100
%
0
684
685
686
687
688
689
690
691
m/z
dd565 12 (0.259) Cm (12:24)
1: TOF MS ES+
5.22e6
685.1346
687.1329
686.1414
688.1358
689.1287
690.1331
100
%
0
684
685
686
687
688
689
690
691
m/z

Fig. S13 ESI-MS of complex **3** in DMSO-acteonitrile as arepresentative of five Ni^{II} complexes: (A) simulated and experimental spectra (B) isotopic distribution pattern.

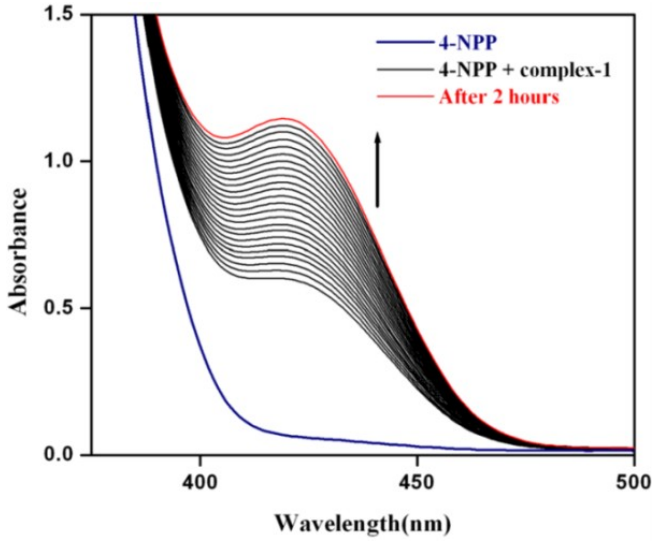

Fig. 14 Wavelength scan for the hydrolysis of 4-NPP in the absence and presence of complex **1** (substrate:catalyst = 20:1) in 75% DMSO (DMSO : pH 9 buffer = 3 :1) recorded at 25 °C at an interval of 10 min for 2 h. [4-NPP] = 1×10^{-3}(M), [Complex **1**] = 0.05×10^{-3}(M). The arrow shows the change in absorbance with reaction time.

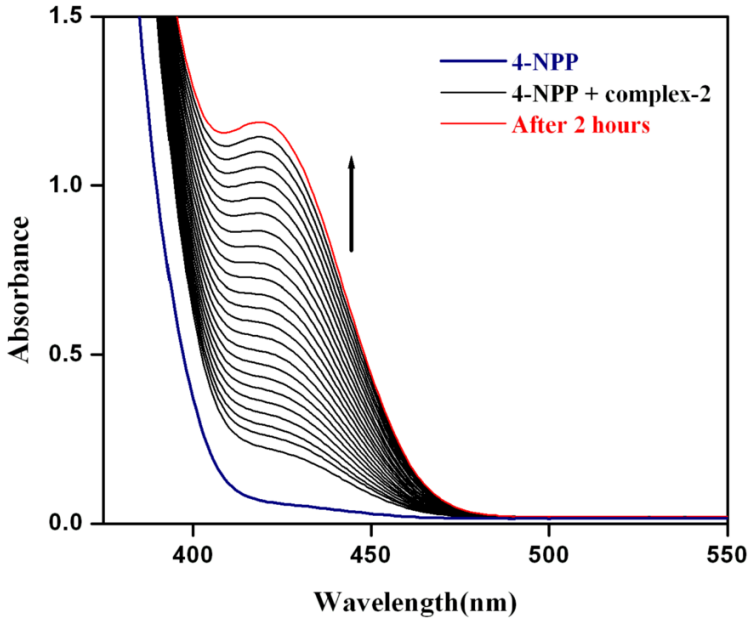

Fig. S15 Wavelength scan for the phosphatase activity of complex **2** in 75% DMSO (DMSO : pH 9 buffer = 3 :1). [4-NPP] = 1×10^{-3}(M), [Complex **2**] = 0.05×10^{-3}(M).

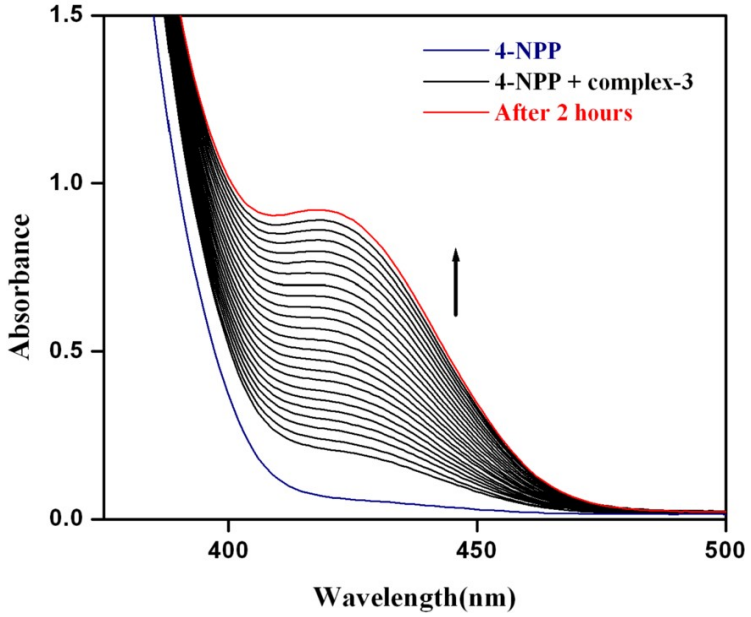

Fig. S16 Wavelength scan for the Phosphatase activity of complex **3** in 75% DMSO (DMSO : pH 9 buffer = 3 :1). [4-NPP] = 1×10^{-3}(M), [Complex **3**] = 0.05×10^{-3}(M).

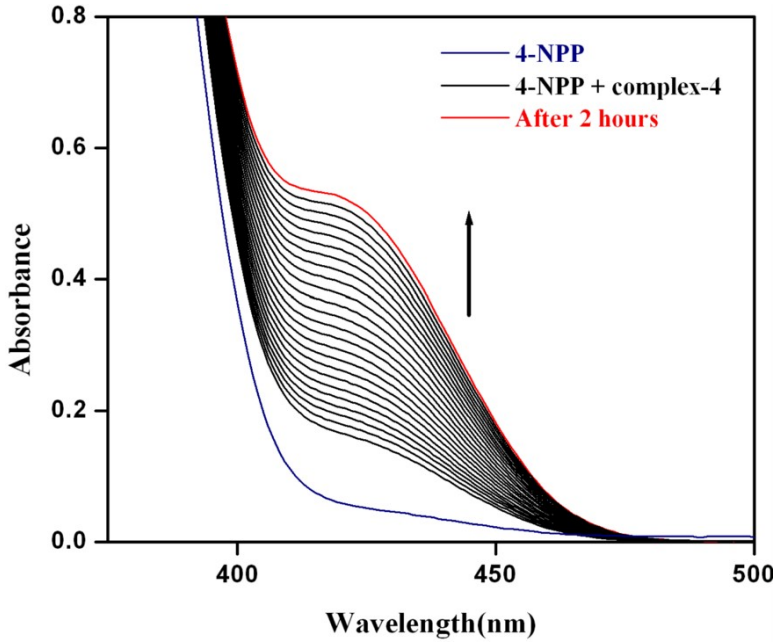

Fig. S17 Wavelength scan for the phosphatase activity of complex **4** in 75% DMSO (DMSO : pH 9 buffer = 3 :1). [4-NPP] = 1×10^{-3}(M), [Complex **4**] = 0.05×10^{-3}(M).

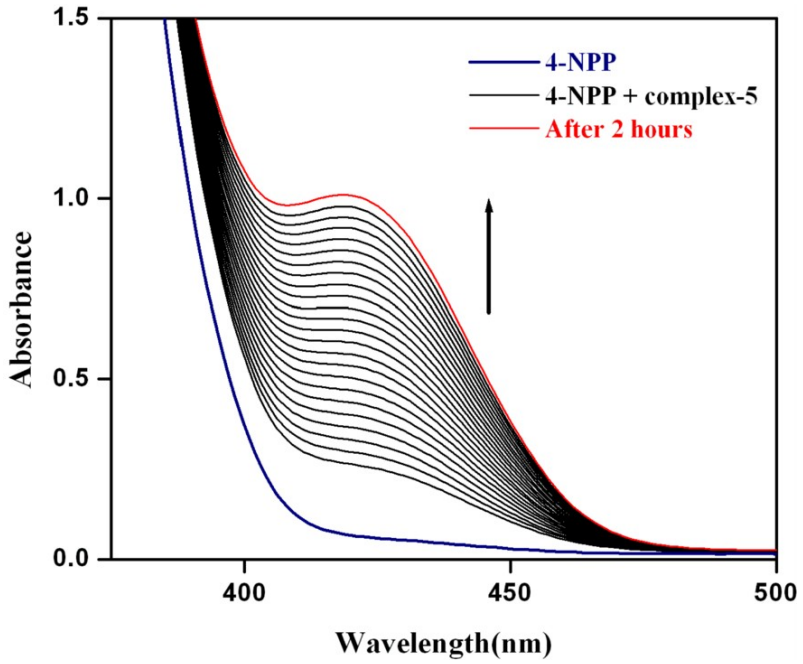

Fig. S18 Wavelength scan for the phosphatase activity of complex **5** in 75% DMSO (DMSO : pH 9 buffer = 3 :1)**.** [4-NPP] = 1 × 10^{-3}(M), [Complex **5**] = 0.05 × 10^{-3}(M).

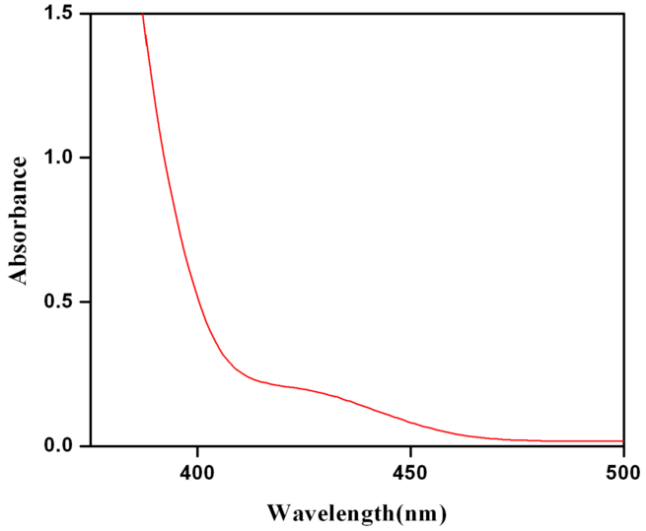

Fig S19 Control experiment against phosphatase activity with ligand HL^1 in 75% DMSO (DMSO : pH 9 buffer = 3 :1) recorded after 2 hours.

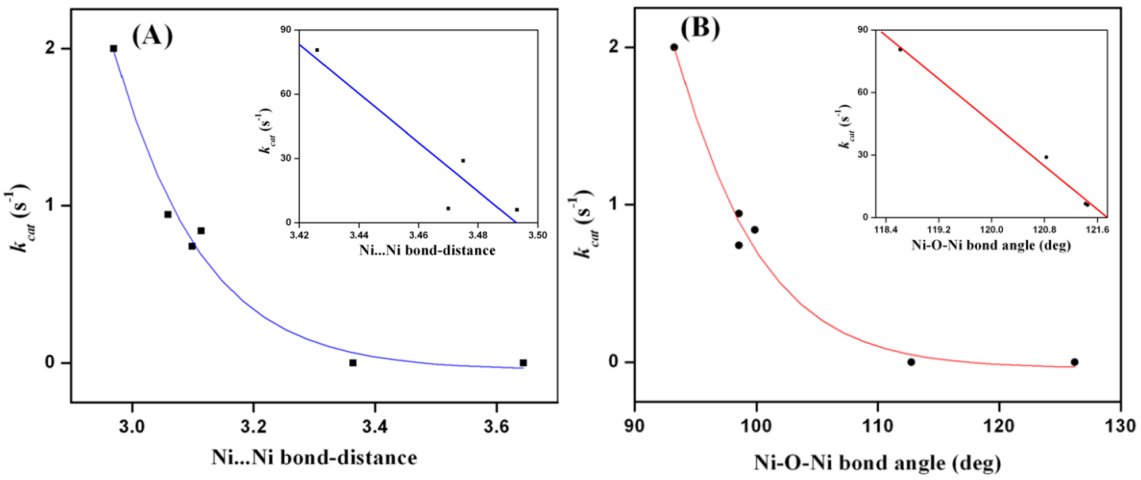

Fig. S20 Interdependence of k_{cat} values with (A) Ni···Ni separation and (B) Ni-O-Ni bond angle of previously reported dinuclear Ni^{II} complexes. Inset shows the same plot for our Ni^{II}complex **1-4** synthesised in this work.

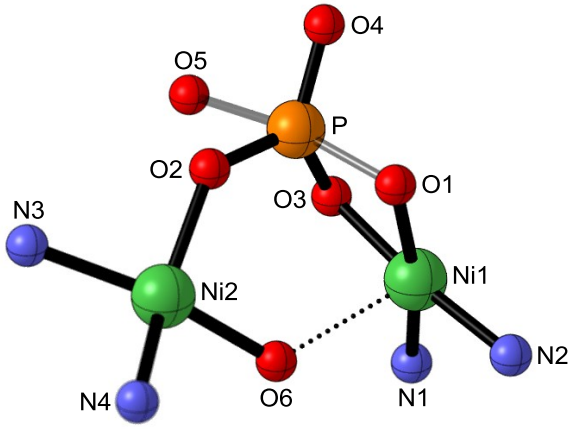

Fig. S21 Depicted are the labels of the atoms in the active catalysis center.

Table S1 Molar conductance values of complex **1-5** in DMSO at 298 K.

Complex	**Molar conductance Λ_M (μS)**	**Nature of electrolyte**
1	98	1:1
2	102	1:1
3	105	1:1

4	90	1:1
5	92	1:1

Table S2 Kinetic parameters for phosphatase activity of complex **1**-**5**.

Complex	10^4 V_{max} ($M\ s^{-1}$)	Standard error	10^3 K_M (M)	Standard error	10^{-4} k_{assoc} (M^{-1})	10^{-3} k_{cat}/k_M ($M^{-1}\ s^{-1}$)
1	3.33	8.62×10^{-4}	5.22	0.016	0.019	1.28
2	14.5	1.17×10^{-3}	30	0.001	33.33	0.97
3	40.3	0.745	69	9.72	0.014	1.17
4	3.04	1.14×10^{-4}	5.62	0.003	0.018	1.08
5	4.1	8.92×10^{-4}	7.6	0.018	0.013	1.08

Table S3 First-order Rate Constants for the Hydrolysis of Various Phosphate Esters by Previously Reported Dinuclear Ni^{II}Complexes.[a]

Complex	Ni…Ni (Å) / Ni-O-Ni(°)	Substrate	Conditions	k_{cat} (s^{-1})	Ref
$[Ni_2(LH_2)(H_2O)_2(OH)(NO_3)](NO_3)_3$ L=Schiff-base	2.970/93.26	4-NPP	MeOH -H_2O (1:1)	2.0	28a
$[Ni_2(L^1)(NCS)_3(H_2O)_2]$, $[Ni_2(L^2)(CH_3COO)(NCS)_2(H_2O)]$, $[Ni_2(L^3)(NCS)_3]$ $L^{1,2,3}$ = Schiff-base	3.114/99.86 3.059/98.54 3.099/98.54	4-NPP	Water-acetonitrile (1:1)	0.841 0.942 0.742	28b
$[Ni_2L(\mu\text{-}OH)]\ (ClO_4)_2$ L = Schiff-base	-	BNPP	Water-ethanol (1:1)	1.49×10^{-4}	4a
$[Ni_2L^{1,2}B](ClO_4)_4$ $L^{1,2}$ =polyazamacrobicyclic B = bipy, phen	-	4-NPP	pH 7.2	(3.36-10.83) $\times\ 10^{-5}$	28c

$[Ni^{II}_2(L^1)(O_2CMe)_2(H_2O)_2][PF_6]_3$ MeOH.$3H_2O$ $[Ni^{II}_2(L^2)(O_2CMe)_2(MeOH)(H_2O)][ClO_4]$ $L^{1,2}$ = Mannich-base	3.644/126.19 ~3.364/112.78	HPNP	MeOH -H_2O (33%, v/v)	16.50×10^{-5} 2.96×10^{-5}	36a

[a] BNPP= bis(4-nitrophenyl)phosphate; HPNP= 2-hydroxypropyl(4-nitrophenyl)phosphate

Table S4 Cartesian coordinates of optimized structures.

Cl-1-H_2O-RC

Ni	2.00429	-1.86358	-0.3216
Ni	-0.22215	1.48401	-0.57682
O	1.39969	0.58473	-0.27997
N	2.29912	-1.77399	1.75411
N	3.9311	-1.67667	-0.75008
N	0.86464	2.74482	-1.69253
N	-1.89566	2.54928	-0.518
C	1.97892	1.30709	0.67701
C	2.38078	2.6287	0.37127
C	2.98789	3.42484	1.34004
H	3.30084	4.44016	1.11256
C	3.20461	2.89568	2.61351
C	2.81102	1.59568	2.93145
H	2.96815	1.22265	3.93965
C	2.18478	0.78597	1.97627
C	1.62096	-0.56707	2.34807
H	1.64916	-0.67349	3.44351
H	0.57985	-0.61947	2.02446
C	1.61815	-2.97768	2.31474
H	1.76127	-3.01667	3.40473
H	2.02325	-3.88556	1.86414
H	0.5581	-2.93079	2.0774
C	3.72381	-1.80089	2.17128
H	3.77904	-2.07468	3.23591
H	4.12844	-0.7906	2.072
C	4.57737	-2.76469	1.33851
H	5.4953	-2.9925	1.89031
H	4.05483	-3.71726	1.18874
C	4.93802	-2.15783	0.01005
C	6.26964	-2.05998	-0.40465
H	7.05275	-2.46785	0.22657
C	6.57371	-1.44381	-1.61483
H	7.60471	-1.35985	-1.94698

C	5.52799	-0.94198	-2.38685
H	5.70853	-0.45795	-3.34101
C	4.22365	-1.08935	-1.92886
H	3.36135	-0.78931	-2.51008
C	2.21209	3.06992	-1.06009
H	2.39161	4.1463	-1.1527
H	2.96714	2.5655	-1.67145
C	1.08513	1.9353	-2.93497
H	0.12908	1.64085	-3.37
H	1.61988	1.02614	-2.6608
H	1.66547	2.52042	-3.66317
C	0.16562	4.01529	-2.02581
H	0.74613	4.53525	-2.80233
H	0.17449	4.64152	-1.12725
C	-1.2754	3.82962	-2.51303
H	-1.58893	4.76038	-2.99726
H	-1.34343	3.03808	-3.26791
C	-2.23582	3.51599	-1.3995
C	-3.44134	4.21244	-1.27519
H	-3.6884	4.97466	-2.00713
C	-4.30696	3.92461	-0.22443
H	-5.24771	4.45773	-0.12225
C	-3.93744	2.94277	0.69207
H	-4.57062	2.67916	1.53219
C	-2.73169	2.27727	0.50881
H	-2.41509	1.47932	1.16657
O	-0.62491	-3.70203	-2.99156
H	-0.5879	-3.61784	-3.95481
H	-1.0987	-2.90287	-2.6517
O	-2.25044	-2.16476	0.62663
P	-1.12418	-1.375	-0.33508
O	-1.12618	0.06103	0.28285
O	0.11956	-2.21531	0.02336
O	-1.58676	-1.42131	-1.78665
C	-3.57306	-1.87795	0.7146
C	-4.26921	-1.06615	-0.19996
C	-4.25517	-2.45869	1.79949
C	-5.62357	-0.8225	-0.00995
H	-3.75087	-0.65102	-1.05472
C	-5.6073	-2.219	1.98748
H	-3.69902	-3.09446	2.48027
C	-6.28319	-1.39075	1.08351
H	-6.17704	-0.20077	-0.70323
H	-6.14439	-2.65578	2.8205
N	-7.69872	-1.11128	1.28808

O	-8.26885	-1.64979	2.24384
O	-8.26256	-0.34221	0.49902
O	1.76373	-2.00587	-2.12113
H	1.01046	-2.60077	-2.28922
O	-2.00199	0.69948	-3.48769
H	-1.84025	-0.05972	-2.86844
H	-2.42002	0.30262	-4.26586
O	0.04153	-5.10616	-0.46336
H	-0.15557	-5.03161	-1.41486
H	0.01584	-4.17317	-0.17897
Cl	3.97382	3.89539	3.8465

Cl-1-H_2O-TS

Ni	1.6057	-2.02473	-0.01423
Ni	0.09661	1.4443	-0.90271
O	1.5803	0.43705	-0.31502
N	2.27823	-1.9218	1.86139
N	3.34707	-2.24389	-0.89145
N	1.29058	2.85311	-1.678
N	-1.52573	2.59848	-0.73477
C	2.30951	1.11336	0.57383
C	2.92197	2.32381	0.16495
C	3.7145	3.06826	1.03522
H	4.1831	3.99204	0.70753
C	3.91742	2.59745	2.33085
C	3.33841	1.40098	2.75065
H	3.50135	1.06304	3.77
C	2.52727	0.64237	1.89582
C	1.84401	-0.59115	2.44128
H	2.01879	-0.64045	3.52467
H	0.76528	-0.54487	2.28956
C	1.5636	-2.9847	2.63681
H	1.93466	-2.99206	3.67136
H	1.73971	-3.96167	2.182
H	0.49579	-2.77027	2.63803
C	3.74602	-2.10239	2.00027
H	3.97772	-2.29944	3.05671
H	4.23339	-1.16344	1.72614
C	4.30339	-3.23512	1.12813
H	5.29466	-3.51131	1.50239
H	3.67765	-4.13221	1.21534
C	4.42293	-2.82588	-0.31707
C	5.60994	-3.00289	-1.03323
H	6.45727	-3.47668	-0.54798
C	5.69378	-2.56992	-2.354

H	6.61128	-2.7049	-2.91953
C	4.58188	-1.95791	-2.93052
H	4.59682	-1.60102	-3.95487
C	3.42833	-1.81521	-2.16866
H	2.52113	-1.36899	-2.55888
C	2.73441	2.66854	-1.27959
H	3.29416	3.57091	-1.55896
H	3.10525	1.83676	-1.88484
C	1.16698	2.58311	-3.14294
H	0.12236	2.56336	-3.45251
H	1.58239	1.59591	-3.34951
H	1.72196	3.34006	-3.71681
C	0.87826	4.24388	-1.35351
H	1.57685	4.9331	-1.85212
H	0.99521	4.37481	-0.27295
C	-0.53853	4.60696	-1.79273
H	-0.65363	5.68536	-1.6392
H	-0.65189	4.44936	-2.87248
C	-1.6556	3.90526	-1.06212
C	-2.8173	4.61502	-0.75018
H	-2.88801	5.66085	-1.03273
C	-3.86593	3.98377	-0.08624
H	-4.77407	4.52875	0.1549
C	-3.71615	2.64726	0.26776
H	-4.48584	2.09618	0.79693
C	-2.53685	1.99085	-0.06923
H	-2.38224	0.94939	0.18455
O	-0.3225	-4.42984	-2.53516
H	-0.55001	-4.5598	-3.46761
H	-1.09404	-3.94757	-2.13192
O	-2.48505	-1.09411	0.85666
P	-0.95798	-1.59166	-0.69155
O	-1.02711	-0.09096	-1.12333
O	-0.13758	-1.90254	0.6147
O	-1.87552	-2.57039	-1.37901
C	-3.79295	-1.11936	0.83232
C	-4.55719	-1.63719	-0.25705
C	-4.52014	-0.57152	1.93745
C	-5.93861	-1.59267	-0.24164
H	-4.02098	-2.07883	-1.08763
C	-5.90119	-0.52919	1.95064
H	-3.9519	-0.17372	2.77453
C	-6.6201	-1.0345	0.8543
H	-6.51457	-1.98725	-1.07097
H	-6.44264	-0.11083	2.79144

N	-8.05698	-0.97129	0.85352
O	-8.63146	-0.45956	1.83198
O	-8.67373	-1.42441	-0.12625
O	0.61841	-1.99353	-1.63335
H	0.50045	-2.89351	-2.03129
O	-1.57793	0.85601	-3.70832
H	-1.482	0.37218	-2.85611
H	-2.33496	0.4466	-4.15205
O	-1.29501	-1.38747	3.36936
H	-2.04481	-1.65165	3.92152
H	-1.6636	-1.31526	2.45133
Cl	4.91563	3.52365	3.44925

Cl-1-H_2O-PC

Ni	1.8054	-1.99461	-0.05027
Ni	0.14788	1.40181	-1.01272
O	1.67395	0.47333	-0.38879
N	2.2439	-1.87475	1.86917
N	3.63234	-2.13611	-0.73086
N	1.28889	2.89601	-1.70365
N	-1.54403	2.41237	-0.87498
C	2.25099	1.18263	0.58827
C	2.79258	2.45232	0.26853
C	3.43373	3.23221	1.22792
H	3.85004	4.2012	0.96731
C	3.54962	2.74304	2.52733
C	3.02137	1.49876	2.86607
H	3.09847	1.15299	3.89276
C	2.35893	0.70338	1.92056
C	1.68495	-0.56522	2.39115
H	1.73969	-0.61101	3.48605
H	0.62723	-0.57336	2.12907
C	1.4936	-2.97315	2.56182
H	1.75196	-2.9678	3.62892
H	1.75963	-3.93848	2.12623
H	0.42423	-2.80026	2.45489
C	3.69429	-1.98716	2.1707
H	3.8122	-2.16662	3.24821
H	4.16431	-1.02749	1.94217
C	4.39757	-3.09858	1.38054
H	5.35284	-3.32457	1.86538
H	3.80988	-4.02497	1.40773
C	4.65791	-2.68863	-0.04573
C	5.91815	-2.82649	-0.6337
H	6.72372	-3.27705	-0.06297

C	6.12765	-2.38243	-1.93661
H	7.10324	-2.48658	-2.4024
C	5.06651	-1.79581	-2.62514
H	5.18089	-1.42721	-3.63887
C	3.83554	-1.69234	-1.9895
H	2.96784	-1.26034	-2.47299
C	2.70282	2.84094	-1.17486
H	3.18936	3.80622	-1.36577
H	3.21524	2.08108	-1.77114
C	1.31938	2.59267	-3.16762
H	0.31183	2.47802	-3.56797
H	1.83695	1.64304	-3.31187
H	1.8571	3.3858	-3.70782
C	0.7288	4.25073	-1.4529
H	1.3845	4.98668	-1.94253
H	0.77566	4.42645	-0.37319
C	-0.69419	4.45568	-1.97098
H	-0.91231	5.52623	-1.8944
H	-0.74774	4.2168	-3.04008
C	-1.76713	3.69981	-1.23018
C	-2.97607	4.32822	-0.93145
H	-3.12431	5.35973	-1.23574
C	-3.97435	3.63393	-0.25
H	-4.91917	4.1159	-0.01573
C	-3.72896	2.31942	0.12962
H	-4.45566	1.72631	0.67396
C	-2.50613	1.73958	-0.19923
H	-2.29832	0.7132	0.09001
O	0.14883	-4.43832	-2.73
H	-0.00404	-4.62202	-3.6689
H	-0.69835	-4.05271	-2.38222
O	-2.77175	-0.97467	1.24772
P	-0.60131	-1.69825	-1.05234
O	-0.85077	-0.20251	-1.36771
O	-0.01628	-1.94425	0.37658
O	-1.57926	-2.66202	-1.65271
C	-4.05323	-1.05114	1.14705
C	-4.68325	-1.48949	-0.06989
C	-4.93411	-0.6648	2.2176
C	-6.05406	-1.5103	-0.20912
H	-4.03394	-1.82106	-0.8754
C	-6.3061	-0.68535	2.07555
H	-4.48473	-0.33746	3.15243
C	-6.88101	-1.09931	0.85757
H	-6.5178	-1.84267	-1.13112

H	-6.95935	-0.38315	2.8864
N	-8.30191	-1.09613	0.7038
O	-9.01077	-0.72572	1.66206
O	-8.79052	-1.45875	-0.38524
O	0.95523	-2.03426	-1.81052
H	0.89172	-2.9386	-2.23387
O	-1.40065	0.86759	-3.91864
H	-1.33723	0.35085	-3.08481
H	-2.20469	0.55347	-4.35746
O	-1.26843	-1.34203	3.46212
H	-1.88951	-1.49781	4.18779
H	-1.84598	-1.21152	2.65336
Cl	4.36039	3.71089	3.7547

Table S5 Structural parameters and NPA atomic partial charge distribution of selected reaction structures. The labels of the atoms are presented in Fig. S27.

Structural Parameters	**Cl-1-H_2O-RC**	**Cl-1-H_2O -TS**	**Me-1-H_2O -TS**	**$CHMe_2$-1-H_2O -TS**	**CMe_3-1-H_2O -TS**	**OMe-1-H_2O -TS**
B(P-O1)	3.45	1.88	1.88	1.88	1.88	1.89
B(P-O5)	1.68	2.23	2.24	2.23	2.23	2.21
A(O1-P-O5)	140.5	165.8	165.7	165.8	165.9	165.8
D(O2-O3-O4-P)	-26.1	7.6	7.9	7.7	7.6	7.1
B(Ni1---Ni2)	4.03	3.89	3.86	3.86	3.86	3.87
B(Ni1-O6)	2.52	2.48	2.47	2.47	2.47	2.47
A(Ni1-O6-Ni2)	132.0	125.1	124.3	124.1	124.6	124.7
Atomic Partial Charge	**Cl-1-H_2O-RC**	**Cl-1-H_2O -TS**	**Me-1-H_2O -TS**	**$CHMe_2$-1-H_2O -TS**	**CMe_3-1-H_2O -TS**	**OMe-1-H_2O -TS**
C(P)	2.568	2.551	2.550	2.549	2.550	2.550
C(O1)	-1.034	-0.972	-0.972	-0.973	-0.972	-0.972
C(O2)	-1.107	-1.141	-1.142	-1.143	-1.143	-1.144
C(O3)	-1.121	-1.036	-1.035	-1.037	-1.037	-1.037
C(Ni1)	0.820	0.777	0.776	0.773	0.776	0.772
C(Ni2)	0.822	0.872	0.864	0.859	0.865	0.860

C(O6)	-0.742	-0.749	-0.755	-0.788	-0.756	-0.788