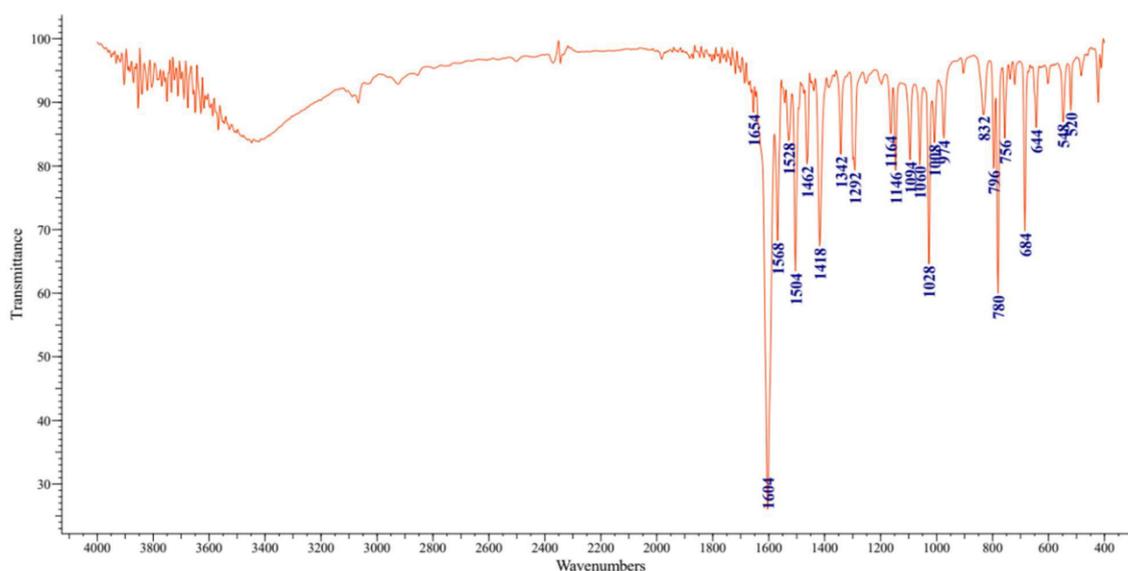
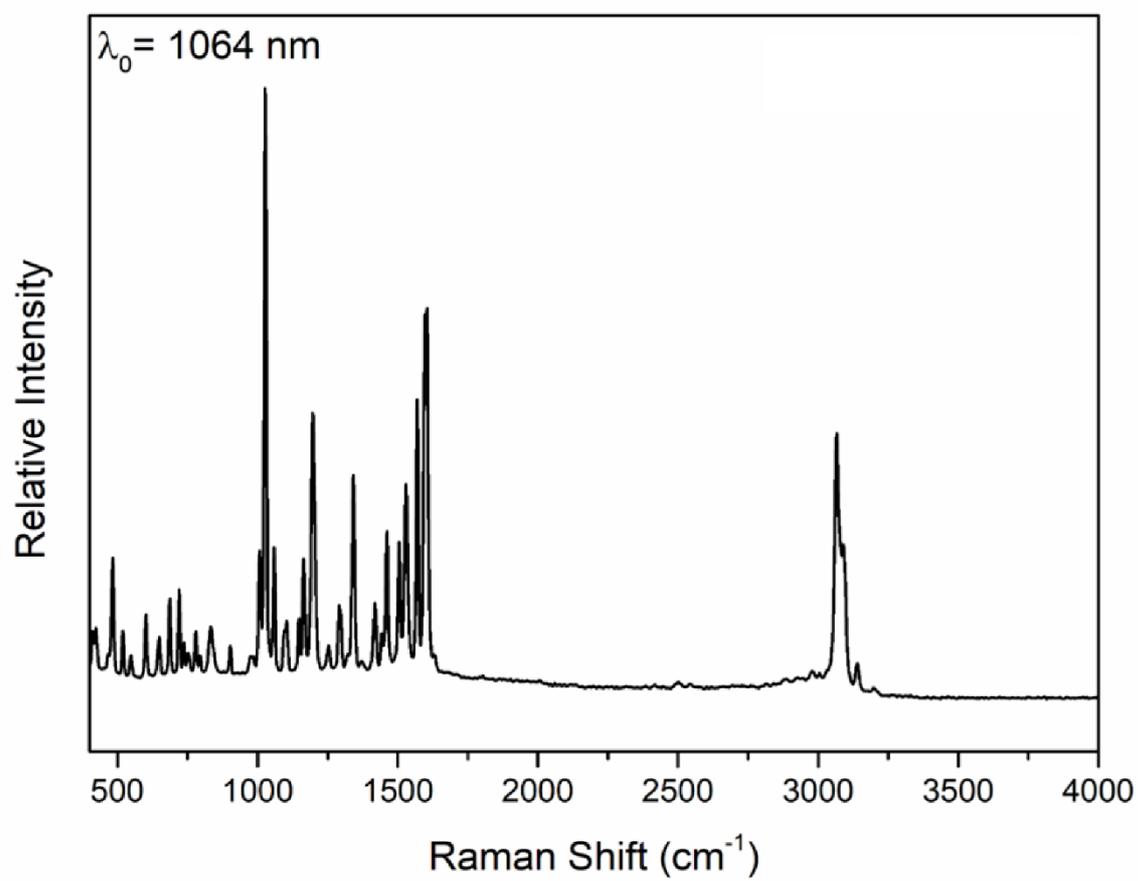


# Supplementary Materials: Reactivity of Coordinated 2-Pyridyl Oximes: Synthesis, Structure, Spectroscopic Characterization and Theoretical Studies of Dichlorodi{(2-pyridyl)furoxan}zinc(II) Obtained from the Reaction Between Zinc(II) Nitrate and Pyridine-2-Chloroxime

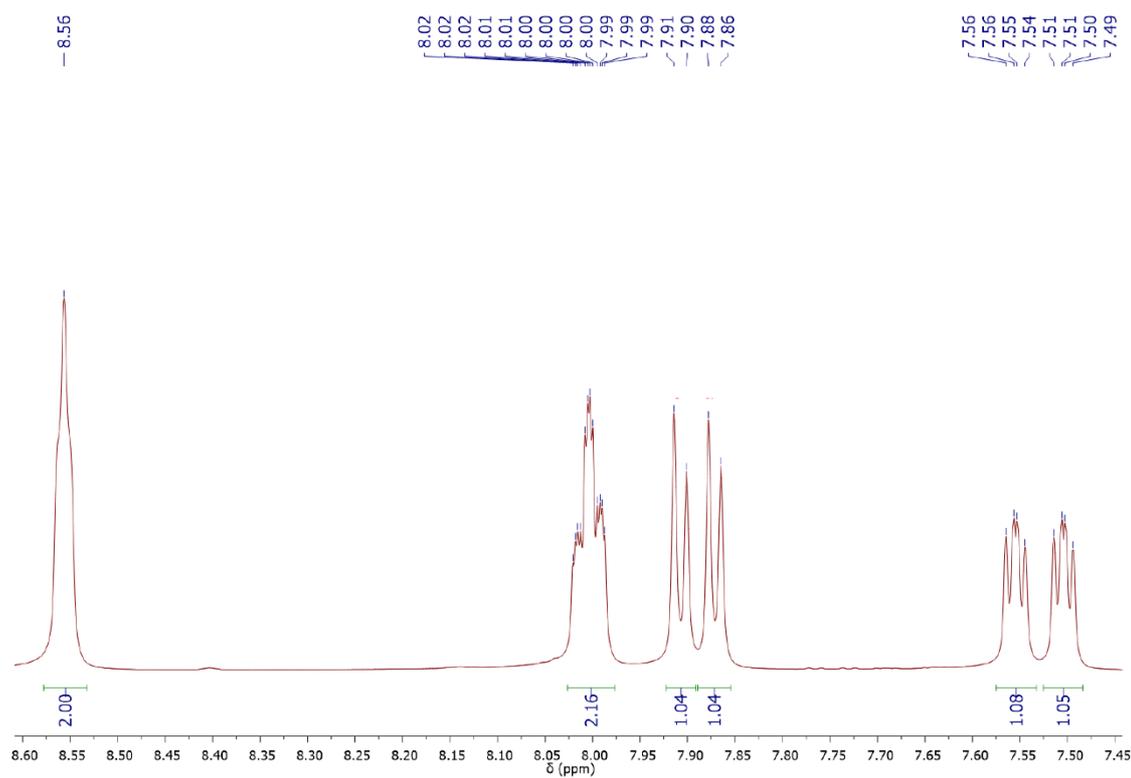
Sokratis T. Tsantis, Vlasoula Bekiari, Demetrios I. Tzimopoulos, Catherine P. Raptopoulou, Vassilis Psycharis, Athanasios Tspis and Spyros P. Perlepes



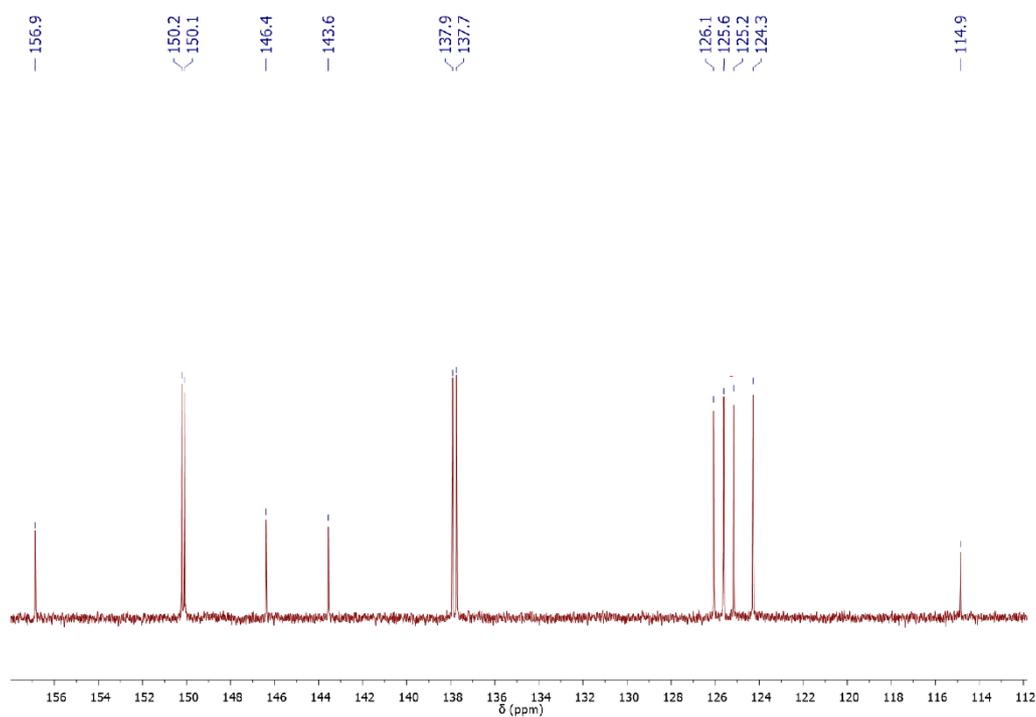
**Figure S1.** The IR spectrum (KBr, cm<sup>-1</sup>) of complex [ZnCl<sub>2</sub>(L)] (1).



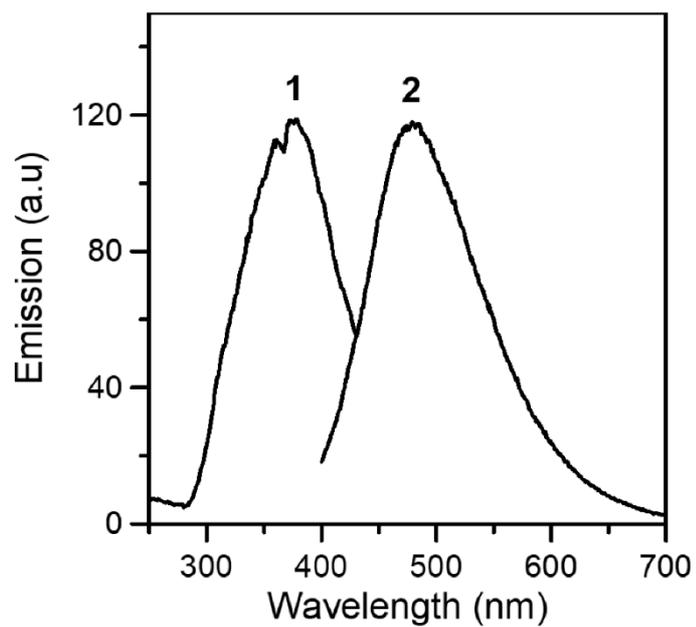
**Figure S2.** The FT-Raman spectrum of complex [ZnCl<sub>2</sub>(L)] (1).



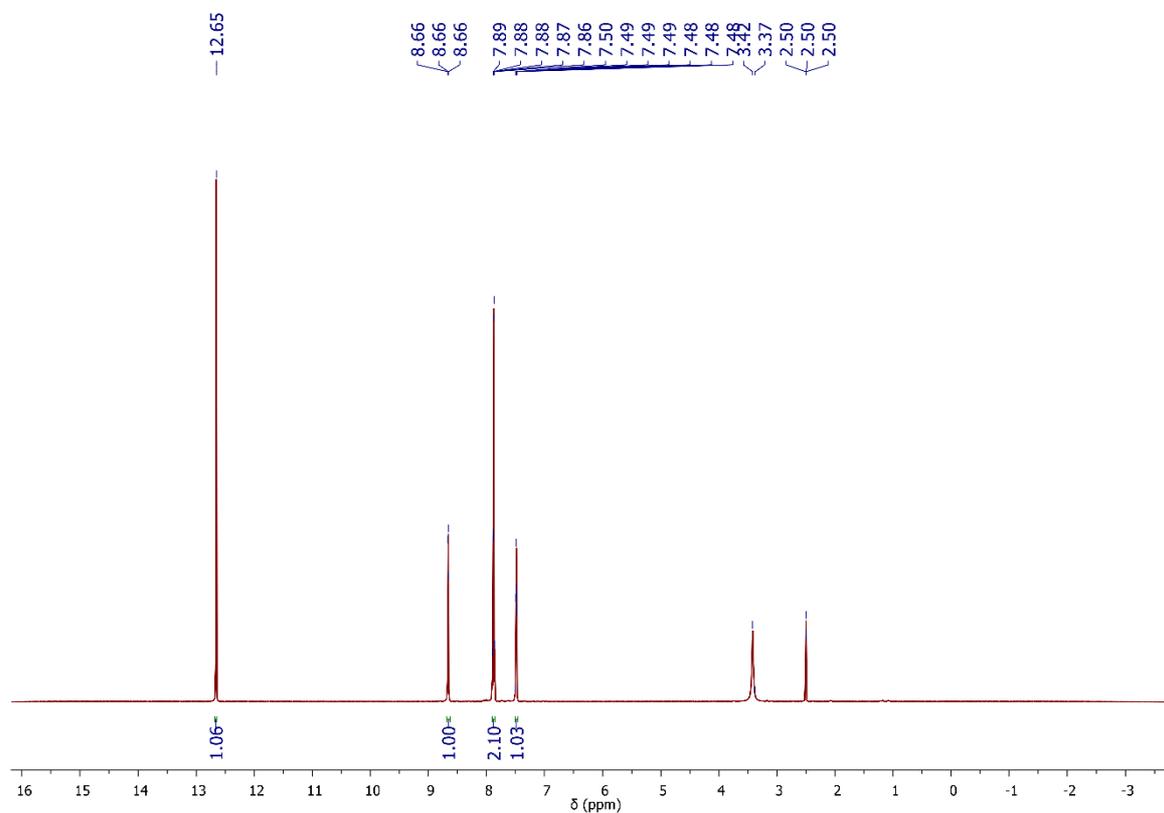
**Figure S3.** The  $^1\text{H}$  NMR spectrum ( $\delta$ , ppm) of complex  $[\text{ZnCl}_2(\text{L})]$  (**1**) in  $d_6$ -DMSO in the aromatic region.



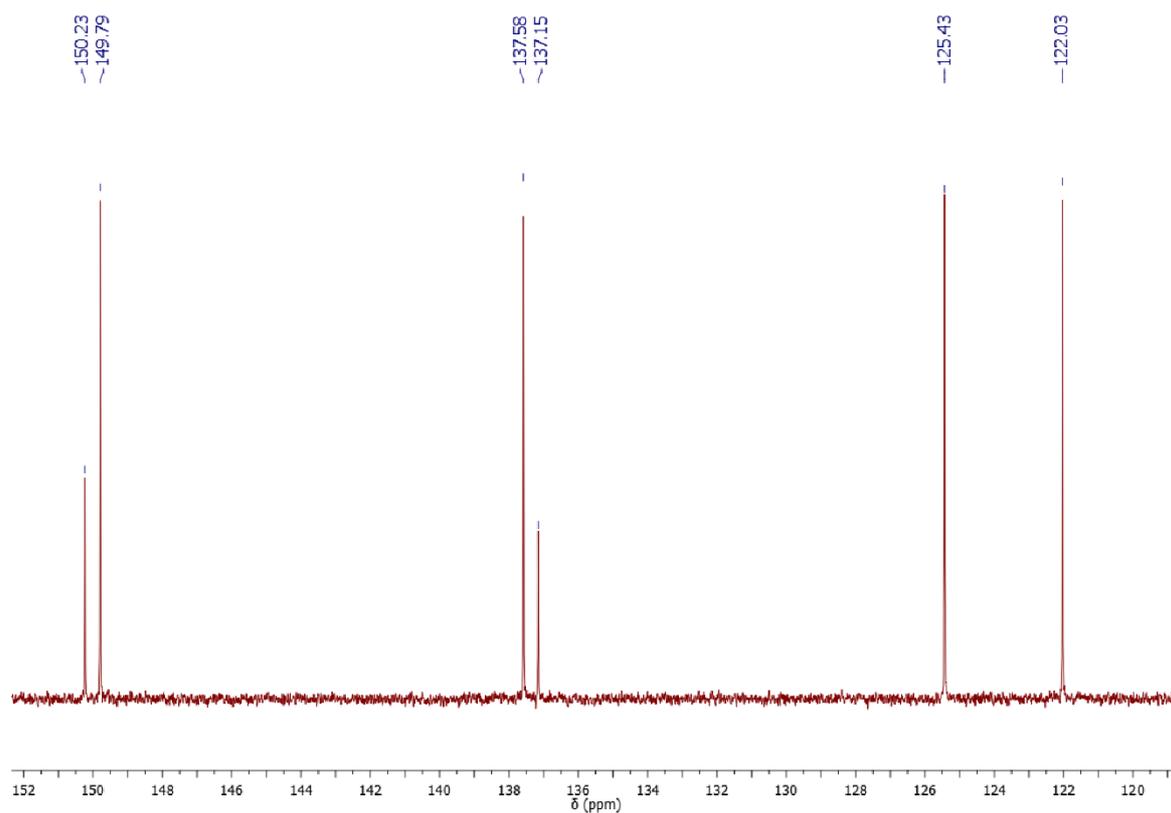
**Figure S4.** The  $^{13}\text{C}$  NMR spectrum ( $d_6$ -DMSO,  $\delta/\text{ppm}$ ) of complex  $[\text{ZnCl}_2(\text{L})]$  (**1**) in the  $\delta$  range 160–112 ppm.



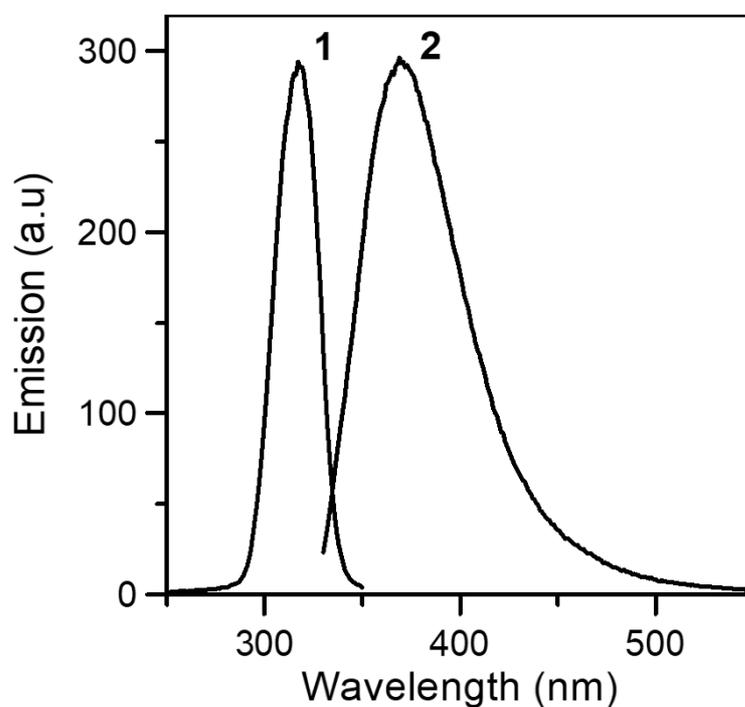
**Figure S5.** Solution (MeOH), room-temperature excitation (curve 1; maximum emission at 479 nm) and emission (curve 2; maximum excitation at 373 nm) spectra of the free ligand L.



**Figure S6.** The <sup>1</sup>H NMR spectrum (*d*<sub>6</sub>-DMSO,  $\delta$ /ppm) of ClpaoH.



**Figure S7.** The  $^{13}\text{C}$  NMR spectrum ( $d_6$ -DMSO,  $\delta$ /ppm) of ClpaoH in the  $\delta$  range 153–120 ppm.



**Figure S8.** Solution (MeOH), room-temperature excitation (curve 1; maximum emission at 369 nm) and emission (curve 2; maximum excitation at 317 nm) spectra of ClpaoH.

**Table S1.** Cartesian coordinates and selected energetic data for the species participating in the reaction of ClpaoH and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in the presence of Et<sub>3</sub>N.

<b>ClpaoH</b>			
C	-3.193893000	-0.083400000	0.001560000
C	-2.523944000	1.116233000	0.205751000
C	-1.131619000	1.120041000	0.208439000
C	-0.462164000	-0.089079000	0.005982000
N	-1.100426000	-1.250460000	-0.195621000
C	-2.431176000	-1.235926000	-0.192921000
C	1.018862000	-0.160657000	0.021150000
Cl	1.905956000	1.336817000	-0.198642000
N	1.624460000	-1.268776000	0.190844000
O	2.974494000	-1.305900000	0.188557000
H	-4.278184000	-0.133943000	-0.011780000
H	-3.071063000	2.041228000	0.363634000
H	-0.585432000	2.042280000	0.371941000
H	-2.917060000	-2.194911000	-0.362040000
H	3.329913000	-0.401976000	0.040380000
Sum of electronic and zero-point Energies=			-875.783196
Sum of electronic and thermal Energies=			-875.774808
Sum of electronic and thermal Enthalpies=			-875.773864
Sum of electronic and thermal Free Energies=			-875.818005
<b>Clpao<sup>-</sup></b>			
C	-3.170918000	-0.055680000	0.007133000
C	-2.468168000	1.144976000	0.067173000
C	-1.079767000	1.123589000	0.062137000
C	-0.406609000	-0.112020000	-0.003208000
N	-1.091433000	-1.274359000	-0.069304000
C	-2.422084000	-1.229232000	-0.059745000
C	1.055685000	-0.195601000	0.002240000
Cl	1.962386000	1.349759000	-0.061405000
N	1.708639000	-1.310538000	0.059512000
O	2.995739000	-1.346343000	0.065972000
H	-4.256214000	-0.087824000	0.009672000
H	-2.994188000	2.095096000	0.120289000
H	-0.520111000	2.050177000	0.112767000
H	-2.925243000	-2.194521000	-0.112448000
Sum of electronic and zero-point Energies=			-875.332305
Sum of electronic and thermal Energies=			-875.324020
Sum of electronic and thermal Enthalpies=			-875.323076
Sum of electronic and thermal Free Energies=			-875.367005

<b>pao</b>			
C	2.709662000	-0.059394000	0.000532000
C	2.070907000	1.176280000	0.000257000
C	0.680598000	1.213479000	-0.000470000
C	-0.007973000	-0.004478000	-0.000868000
N	0.593717000	-1.204939000	-0.000491000
C	1.926004000	-1.214335000	0.000196000
C	-1.441451000	-0.011448000	-0.000338000
N	-2.601853000	-0.008013000	-0.000366000
O	-3.816859000	-0.003805000	0.000938000
H	3.792480000	-0.135265000	0.001182000
H	2.642575000	2.099728000	0.000874000
H	0.137088000	2.152674000	-0.000309000
H	2.393195000	-2.196664000	0.000893000
Sum of electronic and zero-point Energies=			-415.134097
Sum of electronic and thermal Energies=			-415.127062
Sum of electronic and thermal Enthalpies=			-415.126117
Sum of electronic and thermal Free Energies=			-415.166443

<b>[Zn(Cl)pao]<sup>+</sup></b>			
C	-3.250825000	0.400375000	0.043122000
C	-2.745295000	1.706423000	-0.033218000
C	-1.382687000	1.917243000	-0.041366000
C	-0.506736000	0.812735000	0.016115000
N	-1.012480000	-0.441859000	0.070804000
C	-2.350384000	-0.639851000	0.088871000
C	0.920041000	1.024738000	0.012294000
Cl	2.036928000	-0.425138000	0.120671000
N	1.478359000	2.187352000	-0.055517000
O	2.732459000	2.346800000	-0.050334000
H	-4.315960000	0.198913000	0.058978000
H	-3.421437000	2.554803000	-0.085835000
H	-0.959953000	2.912978000	-0.095832000
H	-2.677514000	-1.672581000	0.139802000
Zn	0.250720000	-1.969653000	-0.076259000
Sum of electronic and zero-point Energies=			-2654.213183
Sum of electronic and thermal Energies=			-2654.203341
Sum of electronic and thermal Enthalpies=			-2654.202397
Sum of electronic and thermal Free Energies=			-2654.249643

<b>[ZnCl(pao)]<sup>+</sup></b>			
Zn	-1.223556000	-0.770833000	-0.088545000
Cl	-3.373749000	-0.539920000	0.149097000
N	0.782134000	-0.656268000	-0.081041000
O	-0.339082000	3.849408000	-0.041440000
C	1.484742000	-1.800915000	-0.077240000
H	0.903949000	-2.713359000	-0.152818000
C	2.868554000	-1.833884000	0.021116000
H	3.381089000	-2.789196000	0.022070000
C	3.559713000	-0.632164000	0.123831000
H	4.641318000	-0.618156000	0.213145000
C	2.847118000	0.561492000	0.109763000

H	3.346433000	1.520854000	0.182916000
C	1.456825000	0.519440000	0.003374000
C	0.713507000	1.730455000	-0.020431000
N	0.206084000	2.776508000	-0.029612000
Sum of electronic and zero-point Energies=			-2654.259065
Sum of electronic and thermal Energies=			-2654.248416
Sum of electronic and thermal Enthalpies=			-2654.247472
Sum of electronic and thermal Free Energies=			-2654.298183

**[ZnCl<sub>2</sub>(pao)<sub>2</sub>]**

Zn	-0.273068000	-0.486994000	1.091653000
Cl	-0.994452000	-2.411766000	2.047208000
Cl	0.429263000	1.245533000	2.349593000
N	1.004439000	-1.207629000	-0.459821000
N	-1.944865000	0.169437000	-0.093584000
O	3.890666000	2.192131000	0.952167000
C	0.539569000	-2.262614000	-1.140534000
H	-0.437387000	-2.629062000	-0.840444000
C	1.250723000	-2.880985000	-2.162126000
H	0.820558000	-3.732672000	-2.677710000
C	2.508675000	-2.387700000	-2.491293000
H	3.098189000	-2.845322000	-3.279736000
C	3.008615000	-1.296336000	-1.791062000
H	3.986060000	-0.881062000	-2.010183000
C	2.226793000	-0.729434000	-0.780686000
C	2.733443000	0.386342000	-0.052141000
N	3.320159000	1.268012000	0.425539000
O	1.057886000	3.557253000	-1.171450000
N	0.111943000	2.816076000	-1.047085000
C	-0.783294000	2.089284000	-0.906935000
C	-1.962309000	1.288889000	-0.852499000
C	-3.086738000	1.683675000	-1.581020000
H	-3.050429000	2.589047000	-2.176798000
C	-4.232015000	0.897558000	-1.521633000
H	-5.118264000	1.182946000	-2.080016000
C	-4.218995000	-0.250495000	-0.738386000
H	-5.088465000	-0.894039000	-0.658953000
C	-3.057588000	-0.573343000	-0.044001000
H	-3.001413000	-1.459454000	0.581454000
Sum of electronic and zero-point Energies=			-3529.647536
Sum of electronic and thermal Energies=			-3529.625984
Sum of electronic and thermal Enthalpies=			-3529.625040
Sum of electronic and thermal Free Energies=			-3529.704094

**[ZnCl<sub>2</sub>(pao)<sub>2</sub>]<sup>+</sup>**

Zn	1.000433000	-0.435731000	-1.081951000
Cl	3.043873000	-1.383838000	-1.294411000
Cl	-0.220365000	0.177536000	-2.864795000
N	-0.009210000	-1.504137000	0.457360000
N	1.217110000	1.179624000	0.297830000
O	-4.219889000	-0.512208000	-0.802568000
C	0.681988000	-2.455600000	1.102854000

H	1.682742000	-2.645696000	0.725903000
C	0.166409000	-3.155445000	2.185230000
H	0.768934000	-3.913233000	2.674261000
C	-1.122120000	-2.857119000	2.617769000
H	-1.561029000	-3.379505000	3.462491000
C	-1.849377000	-1.878342000	1.950303000
H	-2.857608000	-1.618040000	2.254203000
C	-1.257669000	-1.226929000	0.867280000
C	-2.031989000	-0.234430000	0.121021000
N	-3.133555000	-0.276866000	-0.346599000
O	-3.160946000	2.220259000	-0.764110000
N	-2.038333000	2.291105000	-0.316156000
C	-1.134789000	1.624979000	0.140687000
C	0.158967000	1.880566000	0.747858000
C	0.274552000	2.848139000	1.746581000
H	-0.606974000	3.378077000	2.090120000
C	1.534915000	3.116217000	2.271044000
H	1.654454000	3.871686000	3.041636000
C	2.628674000	2.399918000	1.798255000
H	3.628581000	2.573795000	2.181059000
C	2.422405000	1.434833000	0.817326000
H	3.241060000	0.838769000	0.424489000
Sum of electronic and zero-point Energies=			-3529.611104
Sum of electronic and thermal Energies=			-3529.590803
Sum of electronic and thermal Enthalpies=			-3529.589859
Sum of electronic and thermal Free Energies=			-3529.663083

#### Final Product (Complex 1)

Zn	-0.983548000	-0.933881000	0.744608000
Cl	-2.547915000	-2.531170000	0.445638000
Cl	-0.076530000	-0.419806000	2.751465000
N	0.636180000	-1.348988000	-0.562220000
N	-1.574167000	0.777841000	-0.332315000
O	3.806960000	0.921019000	0.773119000
C	0.666737000	-2.538381000	-1.175161000
H	-0.202699000	-3.170903000	-1.020592000
C	1.741178000	-2.954162000	-1.952842000
H	1.720286000	-3.930689000	-2.424542000
C	2.825515000	-2.096862000	-2.100345000
H	3.684361000	-2.383883000	-2.699331000
C	2.796410000	-0.854874000	-1.473837000
H	3.621266000	-0.158504000	-1.575637000
C	1.679458000	-0.511501000	-0.714502000
C	1.605858000	0.796746000	-0.055385000
N	2.671316000	1.313762000	0.555881000
O	2.320517000	2.592979000	1.019289000
N	1.043981000	2.848573000	0.670274000
C	0.593301000	1.797962000	0.034247000
C	-0.770042000	1.838664000	-0.525265000
C	-1.191495000	2.972771000	-1.213647000
H	-0.506616000	3.801388000	-1.356571000
C	-2.488766000	3.007648000	-1.717804000

H	-2.840588000	3.879815000	-2.260347000
C	-3.316313000	1.908103000	-1.523553000
H	-4.332070000	1.887344000	-1.903585000
C	-2.818379000	0.813598000	-0.825750000
H	-3.423673000	-0.070110000	-0.645916000
Sum of electronic and zero-point Energies=			-3529.702577
Sum of electronic and thermal Energies=			-3529.683930
Sum of electronic and thermal Enthalpies=			-3529.682986
Sum of electronic and thermal Free Energies=			-3529.751228

## L

N	-2.520408000	-0.375556000	-0.794753000
N	1.534066000	-0.957926000	-0.715762000
O	-2.404543000	2.570391000	0.067865000
C	-3.276016000	-1.473733000	-0.742619000
C	-3.062772000	-2.513894000	0.160625000
C	-2.006250000	-2.403639000	1.059456000
C	-1.208175000	-1.265459000	1.018931000
C	-1.505869000	-0.283043000	0.072455000
C	-0.696866000	0.944690000	0.004415000
N	-1.257931000	2.149456000	0.015164000
O	-0.216227000	3.105677000	-0.010704000
N	0.968362000	2.456174000	-0.039849000
C	0.709529000	1.172800000	-0.025845000
C	1.802615000	0.186182000	-0.075450000
C	3.039166000	0.475128000	0.505327000
C	4.049803000	-0.475369000	0.404316000
C	3.784489000	-1.668377000	-0.260951000
C	2.512693000	-1.859542000	-0.800256000
H	-4.092058000	-1.525088000	-1.460472000
H	-3.712066000	-3.384013000	0.155743000
H	-1.806887000	-3.188067000	1.783993000
H	-0.377408000	-1.137665000	1.705805000
H	3.195702000	1.415321000	1.024523000
H	5.025225000	-0.288251000	0.844146000
H	4.541510000	-2.440179000	-0.360374000
H	2.269436000	-2.780101000	-1.326670000
Sum of electronic and zero-point Energies=			-830.320289
Sum of electronic and thermal Energies=			-830.306964
Sum of electronic and thermal Enthalpies=			-830.306020
Sum of electronic and thermal Free Energies=			-830.362479

