Electronic Supplementary Information

Improving the stability and inertness of Cu(II) and Cu(I) complexes with methylthiazolyl ligands by tuning the macrocyclic structure

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Contents: Figures and Tables not shown in the main text **Page**

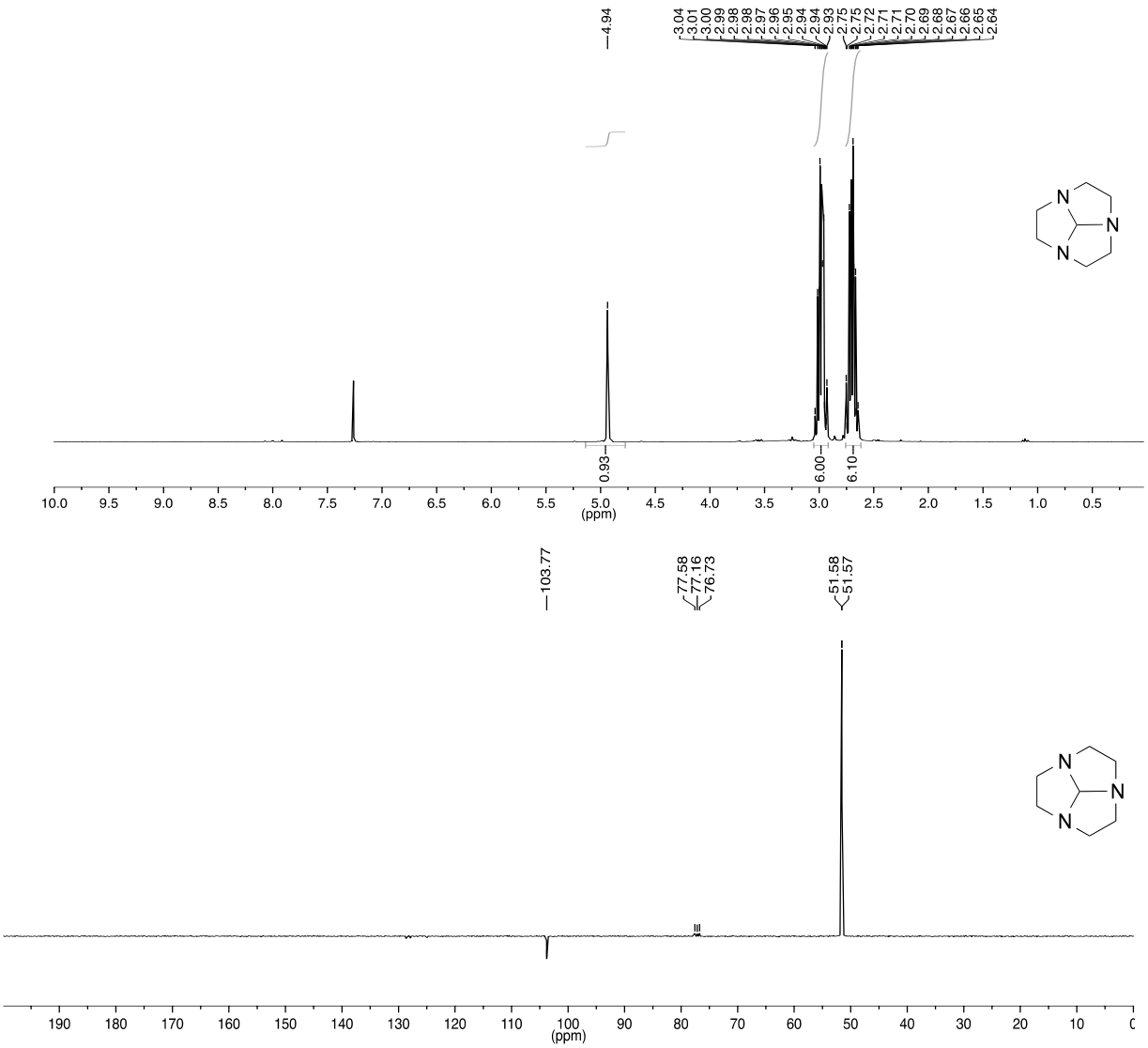


Figure S1: ^{1}H and ^{13}C NMR spectra of **1** in $CDCl_3$ at 25 °C (300MHz).

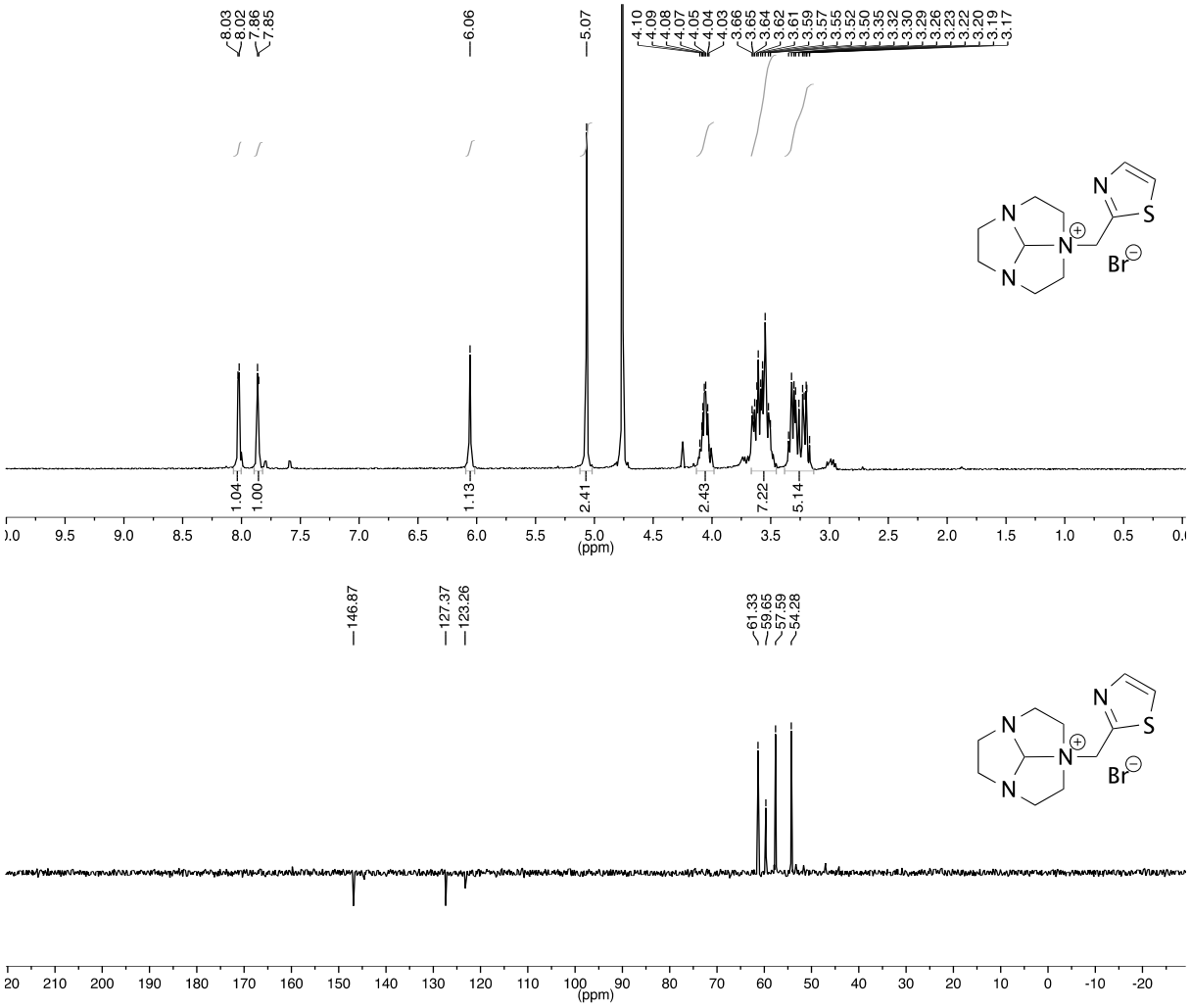


Figure S2: ^{1}H and ^{13}C NMR spectra of **3** in D_2O at 25 °C (300 MHz). Traces of hydrolysis of the orthoamide function in D_2O was observed on the NMR spectra.

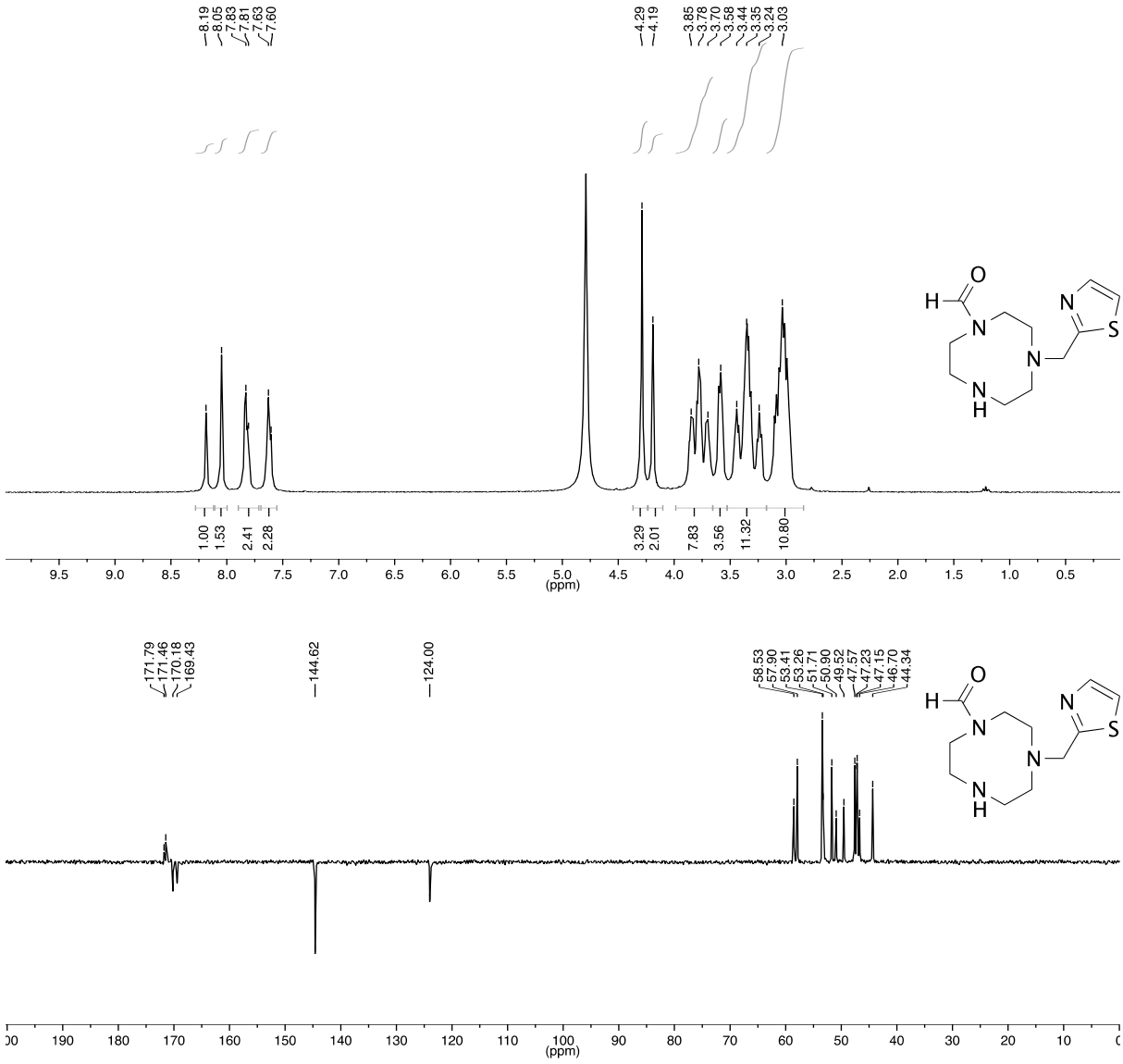


Figure S3: ^{1}H and ^{13}C NMR spectra of **4** (2 rotamers) in D_2O at 25 °C (300MHz).

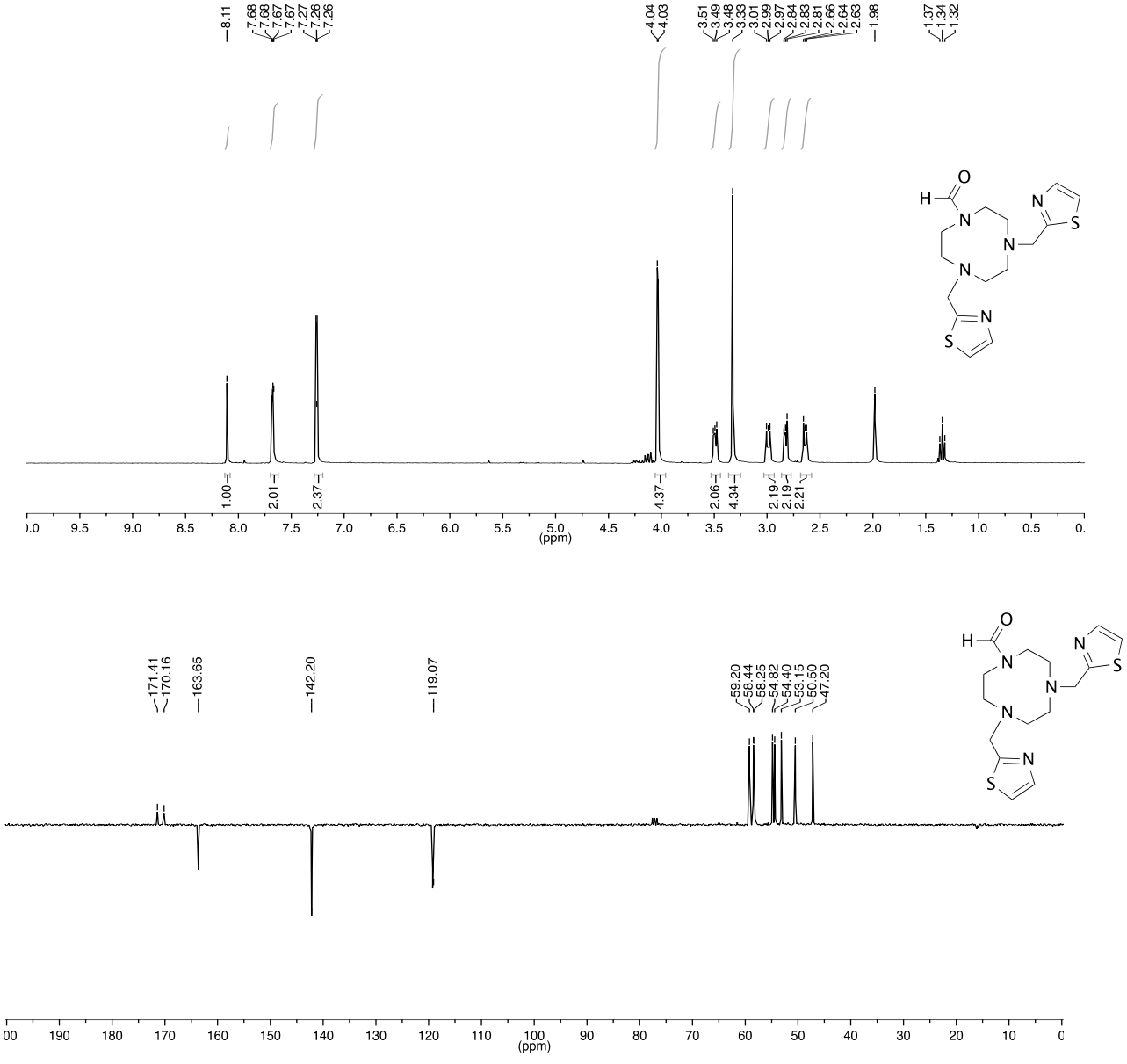


Figure S4: ^{1}H and ^{13}C NMR spectra of **5** in $CDCl_3$ at 25 °C (300 MHz).

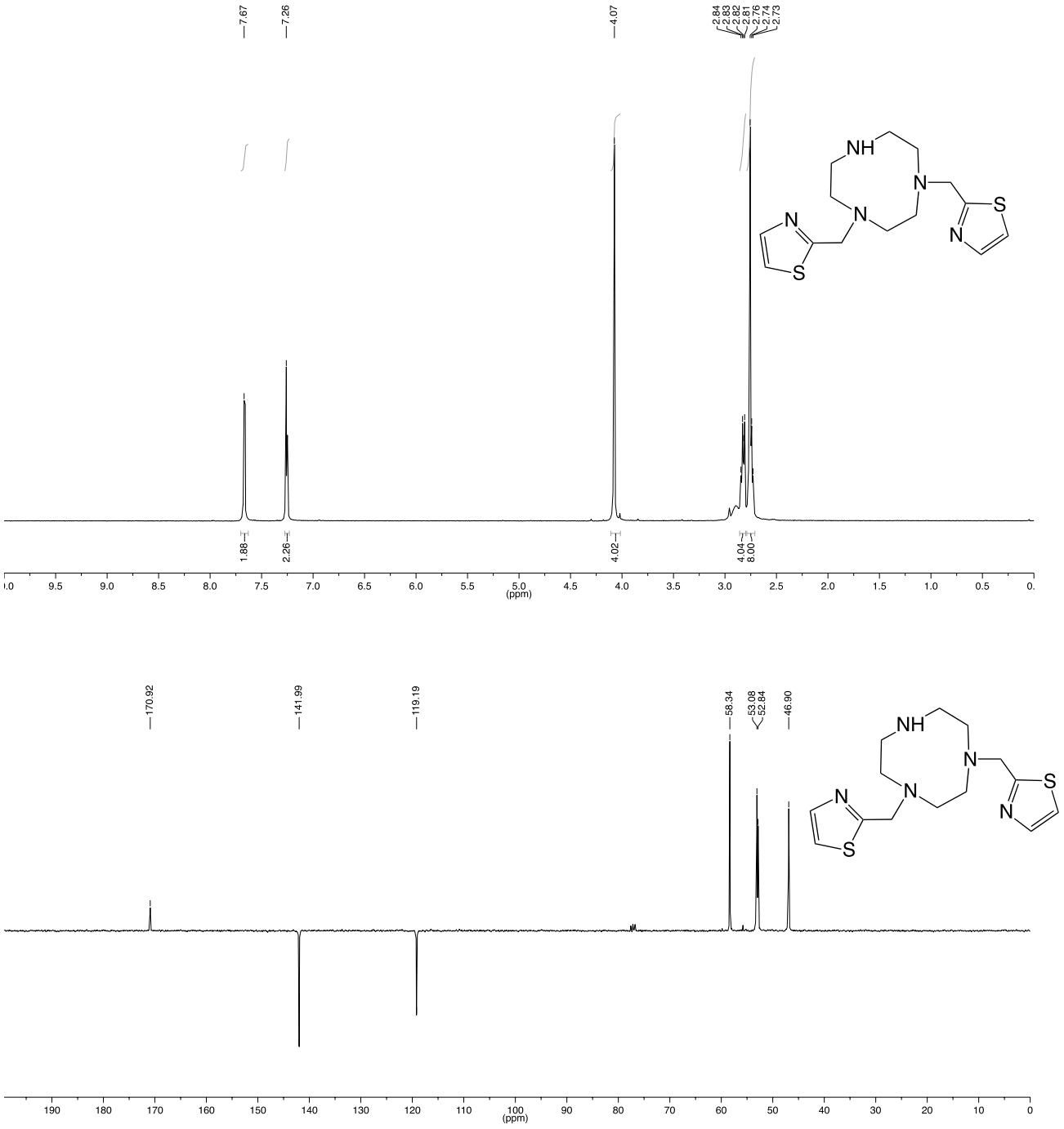
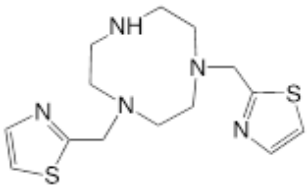


Figure 5: ^{1}H and ^{13}C NMR spectra of **no2th** ligand in $CDCl_3$ at 25 °C (300MHz).



Fédération de Recherche Physique et Chimie du Vivant (FR2708 : CBM/ICOA)
Plate-forme de Spectrométrie de Masse Haute Résolution

HRMS

Analysis Info

Sample Name	**MLF20**	Acquisition Date	01/04/2014 22:53:36
Analysis Name	X013471CYC.d	Laboratory	
Method	Positif.m	Instrument / Ser#	maXis 255552.00086

Acquisition Parameter

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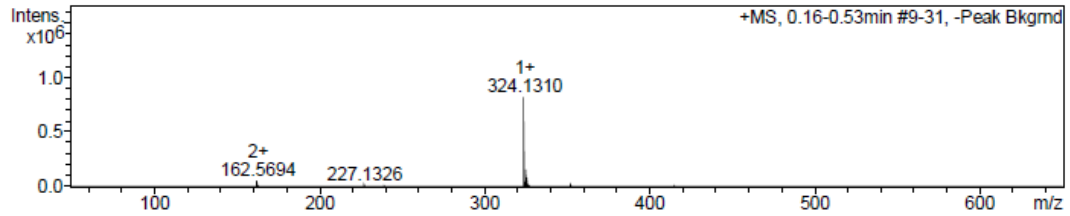

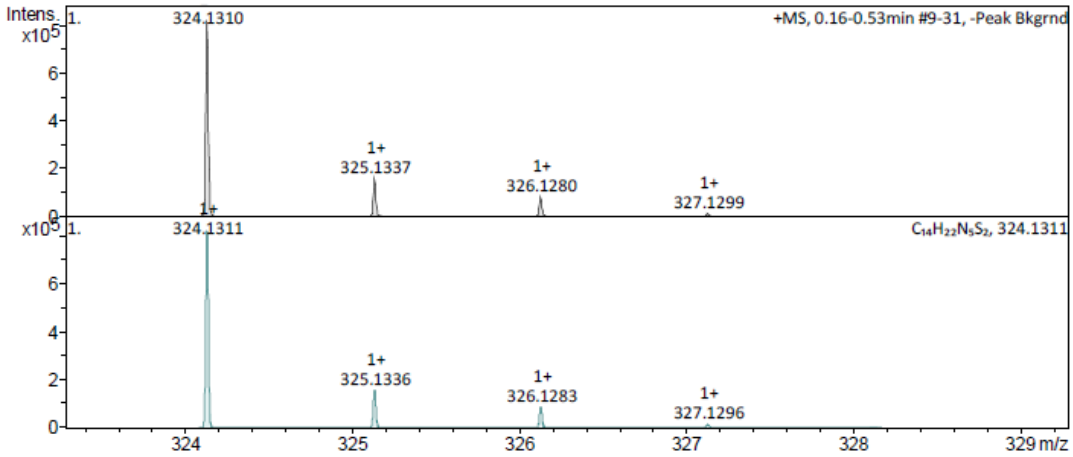

Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e¯ Conf
162.569395	2+	1	C14H23N5S2	162.569195	-1.2	3.4	6.0	even
324.131045	1+	1	C14H22N5S2	324.131114	0.2	2.6	6.5	even

Figure S6. HRMS spectra of **no2th**.

Fédération de Recherche Physique et Chimie du Vivant (FR2708 : CBM/ICOA)
Plate-forme de Spectrométrie de Masse Haute Résolution

HRMS

Analysis Info

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Method	Positif.m	Instrument / Ser#	maXis 255552.00086

Acquisition Parameter

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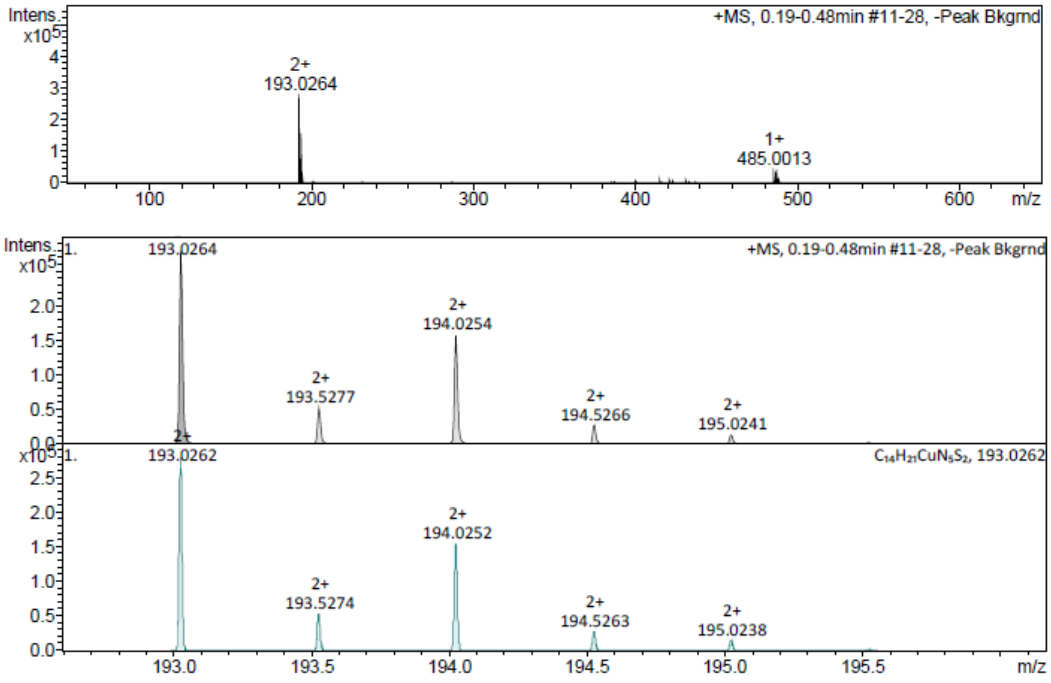
Scan End	3000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Waste



Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e¯ Conf
193.026427	2+	1	C14H21CuN5S2	193.026169	1.3	5.2	6.5	odd
485.001262	1+	1	C14H21ClCuN5O4S2	485.001398	-0.3	9.5	6.0	odd

Figure S7. HRMS spectra of [Cu (**no2th**)]$(ClO_4)_2$.

Fédération de Recherche Physique et Chimie du Vivant (FR2708 : CBM/ICOA)
Plate-forme de Spectrométrie de Masse Haute Résolution

HRMS

Analysis Info

Acquisition Date 04/06/2014 17:01:26

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Analysis Name X014545CYC.d
Method Positif.m

Laboratory
Instrument / Ser# maXis 255552.00086

Acquisition Parameter

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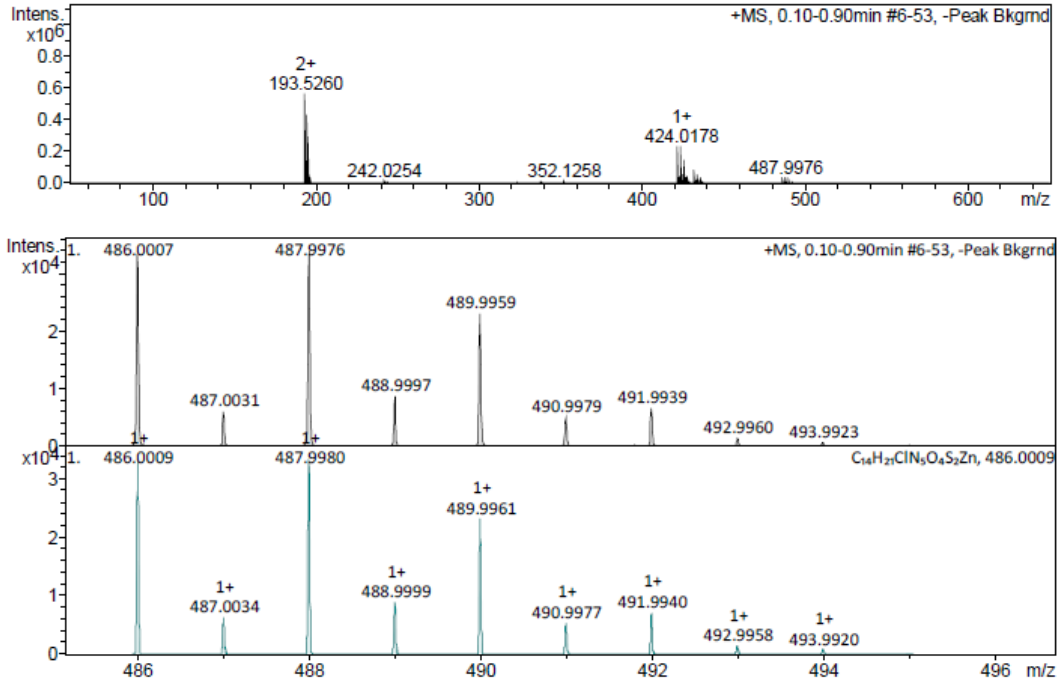

Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
193.525999	2+	1	C14H21N5S2Zn	193.525941	0.3	36.3	7.0	even
422.020794	1+	1	C14H21ClN5S2Zn	422.021284	1.2	20.5	6.5	even
	1+	2	C13H25ClNO4S2Zn	422.019947	2.0	22.1	1.5	even
486.000652	1+	1	C14H21ClN5O4S2Zn	486.000942	-0.6	10.6	6.5	even

Figure S8. HRMS spectra of [Zn(**no2th**)]$(ClO_4)_2$.

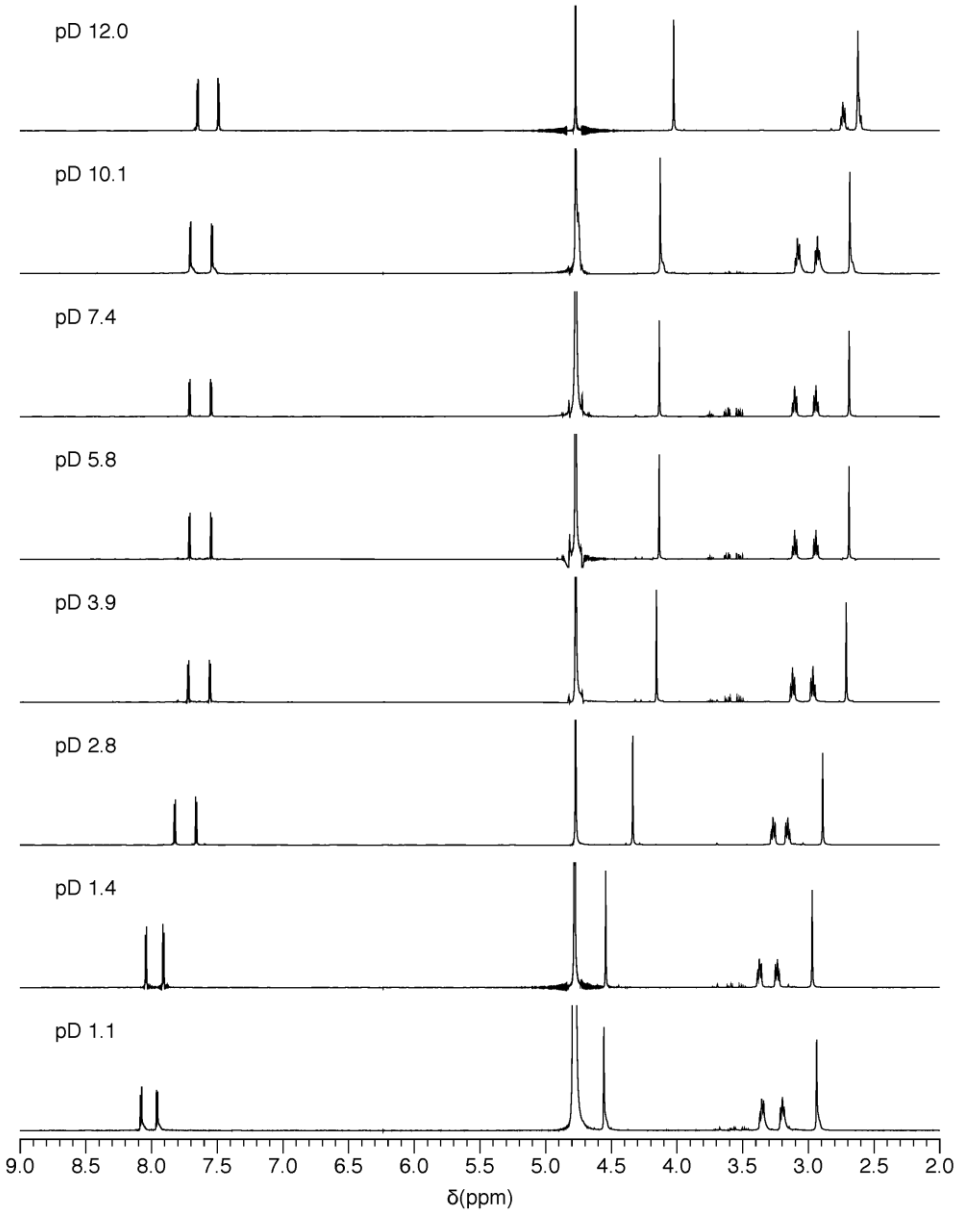

Figure S9. ^{1}H NMR study at various pH (by addition of NaOD or DCl) to **no2th** (300 MHz, 298 K).

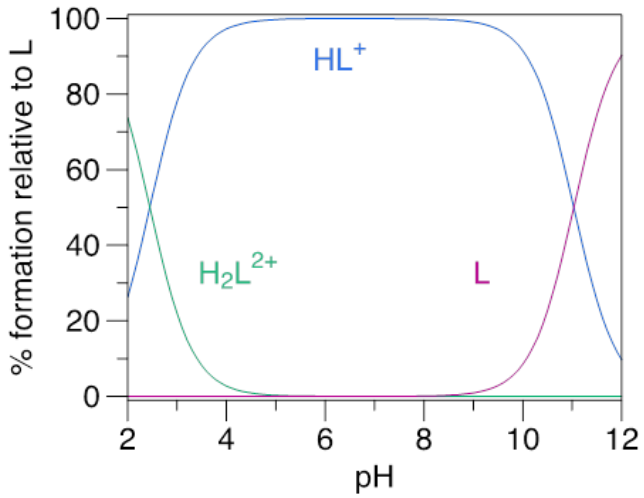

Figure S10. Speciation diagram of the protonated species of **no2th** in aqueous solution. C_L = 1.84×10^{-3} M.

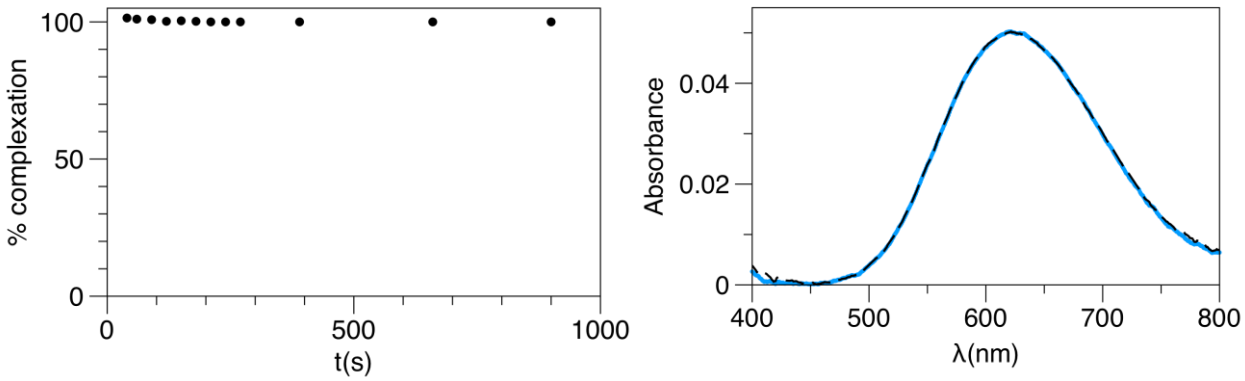

Figure S11: Time course, absorbance in function of time, of complexation of Cu^{2+} with **no2th**. C_L = 3.75×10^{-3} M, C_{Cu} = 0.9 equiv. at pH 2.11 in HCl/KCl buffer at r.t., followed by the increasing complex absorbance band respectively at 620 nm.

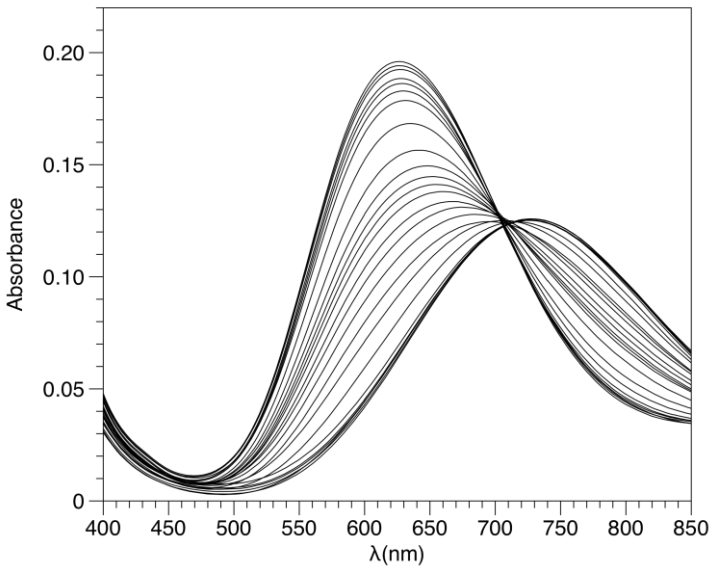

Figure S12. UV-vis titration of a solution of **no2th**, H_4edta, and Cu^{2+} at 1:4:1 ratio with KOH.

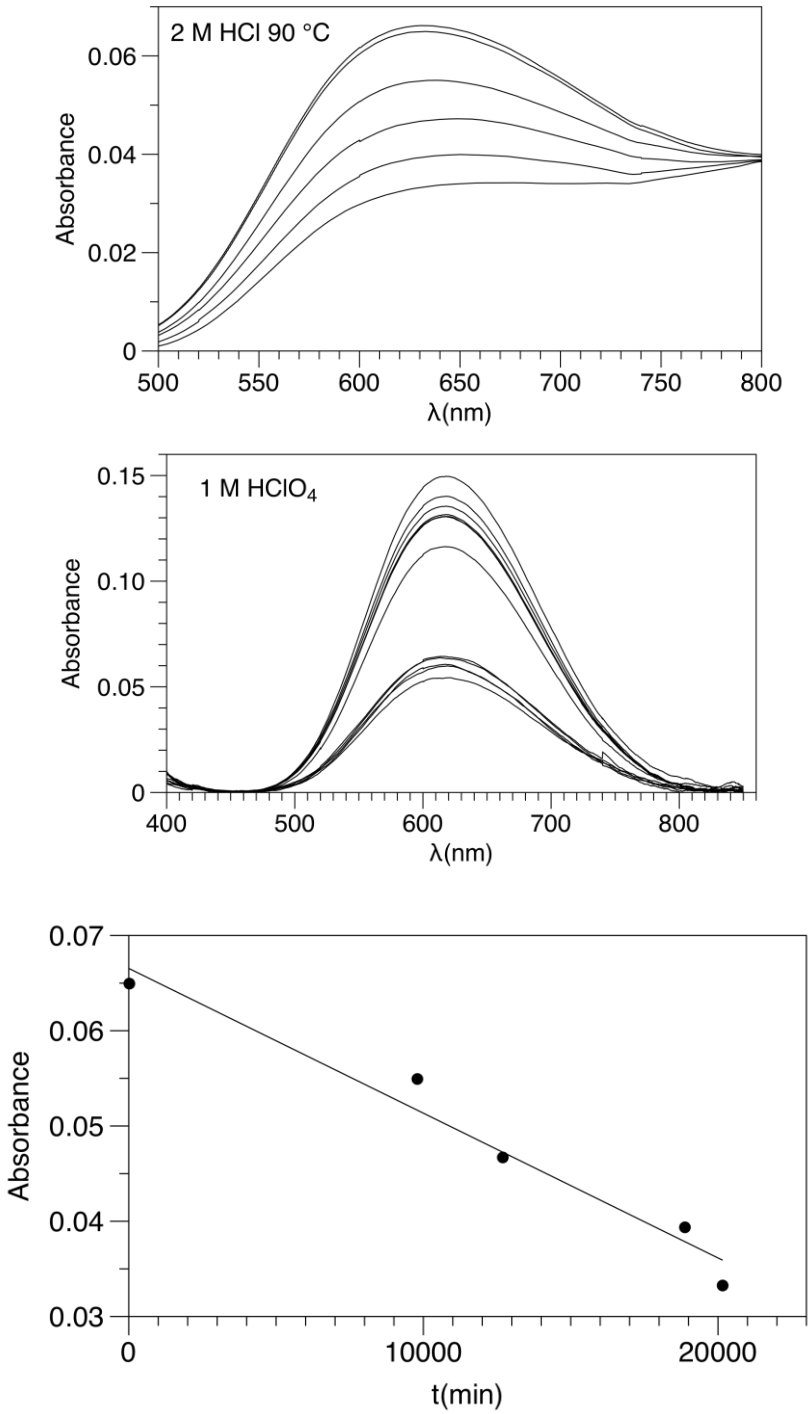

Figure S13: Acid-assisted dissociation of [Cu-**no2th**]$^{2+}$ in 2M HCl and 1M $HClO_4$ and curve Abs = f(t) at 90 °C.

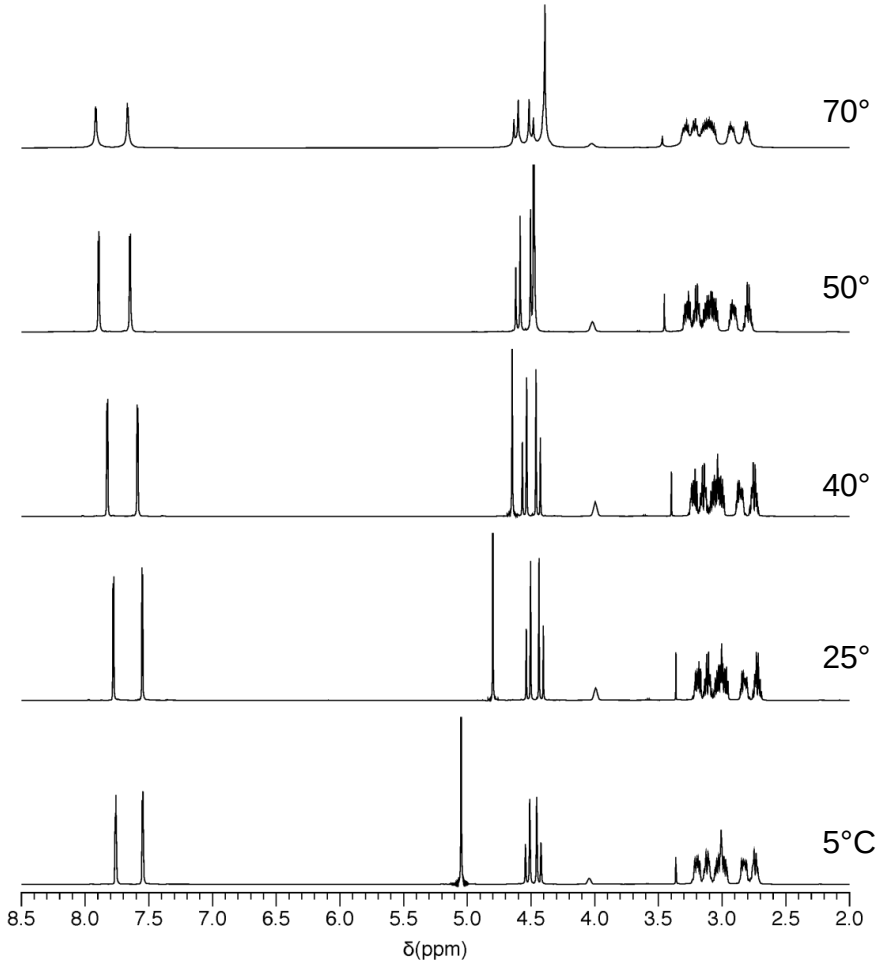

Figure S14. ^{1}H NMR study at various temperatures of [Zn(**no2th**)]$(ClO_4)_2$ in D_2O (500 MHz).

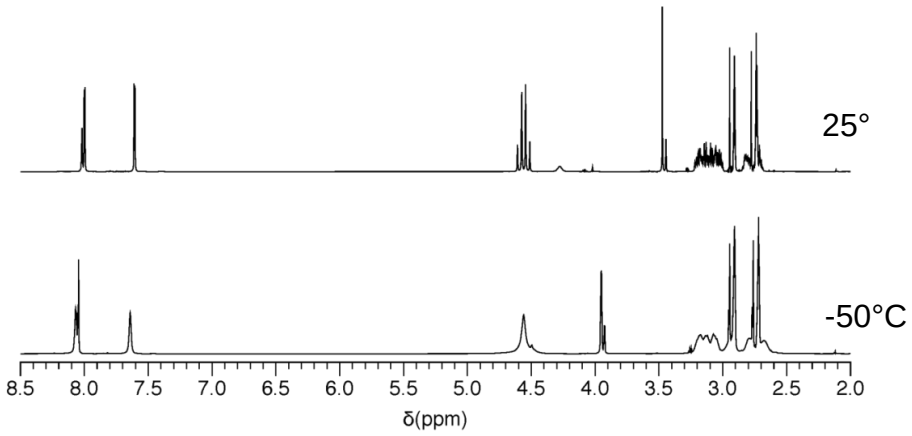

Figure S15. ^{1}H NMR study at 25 and -50 ºC of [Zn(**no2th**)]$(ClO_4)_2$ in DMF-d7 (500 MHz).

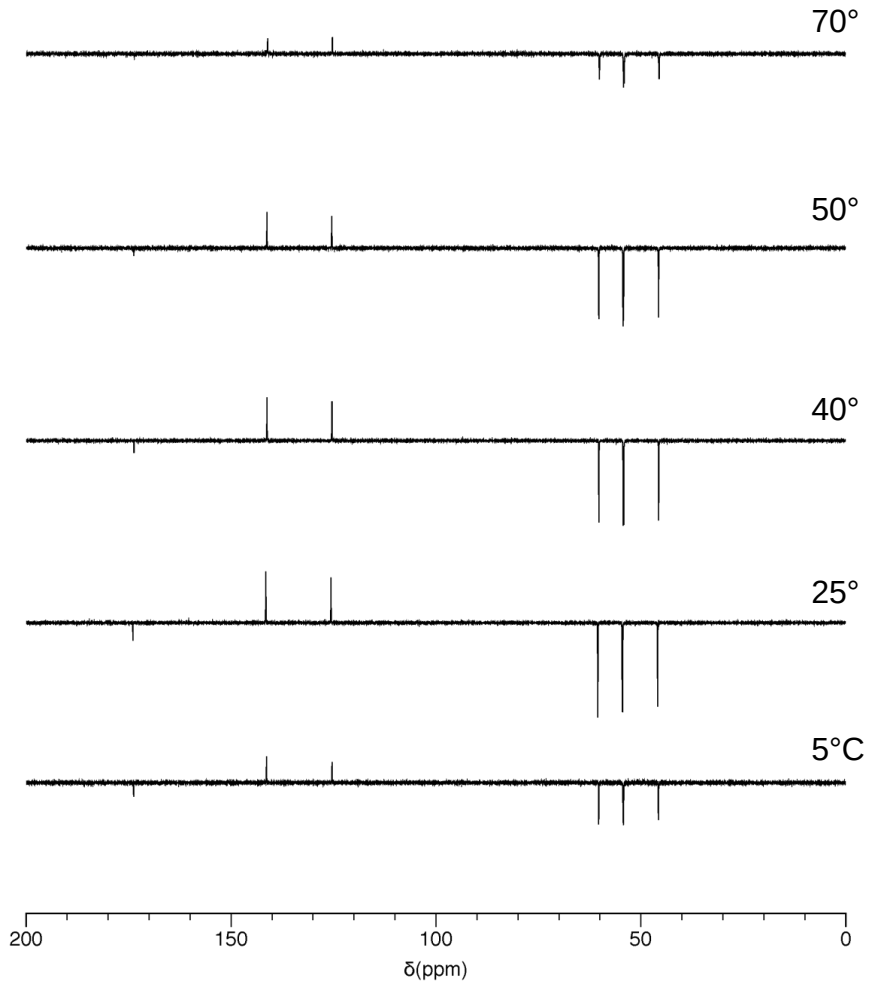

Figure S16. ^{13}C NMR study at various temperatures of [Zn(**no2th**)]$(ClO_4)_2$ in D_2O (125.7MHz).

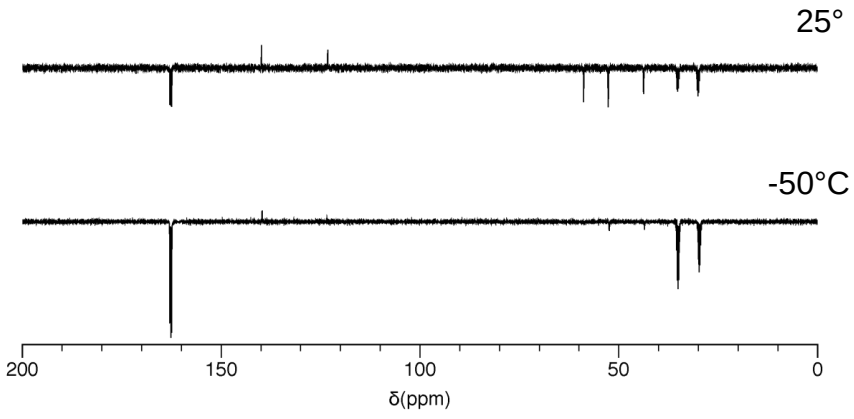

Figure S17. ^{13}C NMR study at various temperatures of [Zn(**no2th**)]$(ClO_4)_2$ in DMF-d_7 (125.7 MHz).

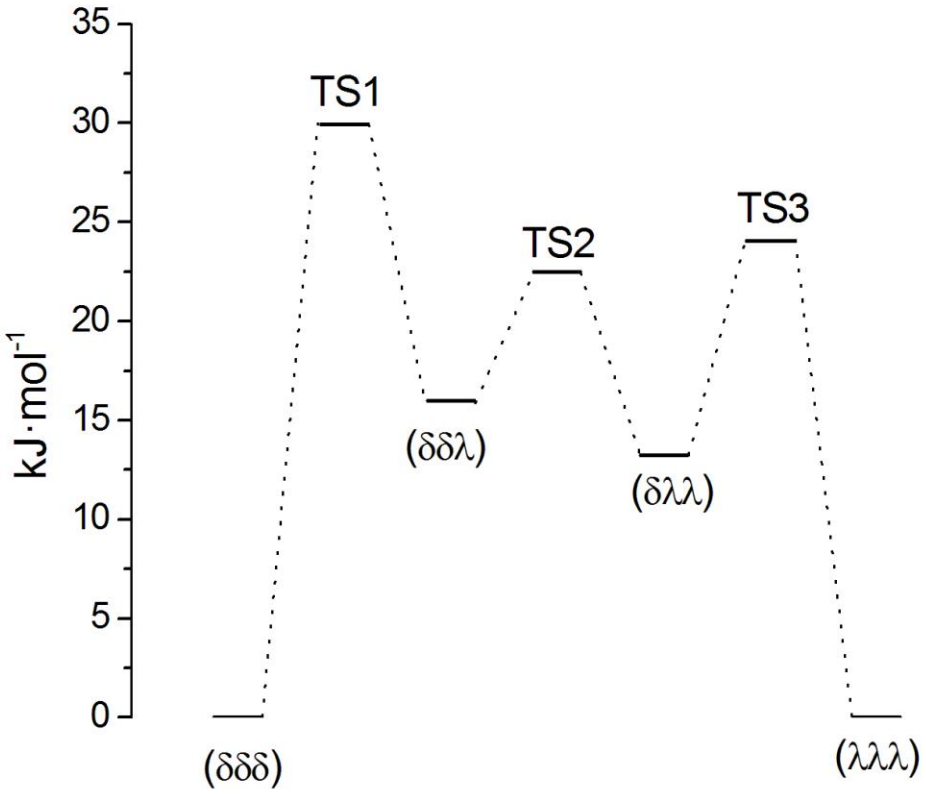

Figure S18: Energies of the minima, transition states (TS) and intermediates involved in the δδδ ↔ λλλ interconversion process of [Zn(**no2th**)]$^{2+}$ as calculated using DFT calculations in aqueous solution at the TPSSh/TZVP level.

(δδδ)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies

	X	Y	Z
C	-0.93674700	-2.48947200	1.23477200
H	-0.67982500	-3.37874500	0.66082900
H	-1.64712500	-2.81413300	1.99899300
C	0.30429300	-1.91298500	1.92093100
H	0.79884100	-2.70342300	2.49611700
H	0.01153000	-1.12206100	2.61386900
C	1.82078500	-2.30966100	-0.00051000
H	1.31351600	-3.25981500	0.16330000
H	2.87228100	-2.47334400	0.24729300
C	1.71898700	-1.91062800	-1.47626700
H	1.98960400	-2.77447800	-2.09069400
H	2.41278200	-1.10303800	-1.70791500
C	-0.69319900	-2.48629900	-1.80399800
H	-0.99768700	-2.71813200	-2.82518500
H	-0.25686100	-3.39653100	-1.39178600
C	-1.92839300	-2.06493600	-1.00632700
H	-2.60532400	-2.92009200	-0.89963200
H	-2.45996200	-1.27892900	-1.54830800
C	-2.68828900	-0.78431200	0.93696200
H	-3.63750500	-1.30614900	0.77969800
H	-2.51661900	-0.73387000	2.01492600
C	-2.75707500	0.62162000	0.40796000
C	-3.25645900	2.92085100	-0.23729800
H	-3.71773600	3.87484200	-0.43644200
C	-1.98039700	2.52843600	-0.47232600
H	-1.20225200	3.13372800	-0.91086300
C	2.24825800	-0.44391000	1.56158900
H	1.82363200	-0.01486700	2.47296800
H	3.13898100	-1.01065800	1.84641200
C	2.60105400	0.68342200	0.62998700
C	3.49956100	2.56957200	-0.62918900
H	4.10868000	3.36067000	-1.03635900
C	2.24158200	2.19918500	-0.97624700
H	1.63506900	2.65420200	-1.74461000
N	-1.55862500	-1.50095500	0.31599200
N	1.22472800	-1.30065900	0.92817700
N	0.35513500	-1.42099000	-1.81227200
H	0.38842200	-0.99390100	-2.73359000
N	-1.70739100	1.22772200	-0.10152400
N	1.74265400	1.13363500	-0.25714000
S	-4.16394700	1.61937600	0.46305100
S	4.09670500	1.54532500	0.63681900
Zn	-0.04186100	0.02156500	-0.32066000

E(RTPSSh) = -3395.8039525 Hartree

Zero-point correction =	0.356095
Thermal correction to Energy =	0.375731
Thermal correction to Enthalpy =	0.376675

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 Thermal correction to Gibbs Free Energy =         0.309131
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3395.447858
 Sum of electronic and thermal Energies =             -
3395.428221
 Sum of electronic and thermal Enthalpies =           -
3395.427277
 Sum of electronic and thermal Free Energies =        -
3395.494821
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TS1-(δδX)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 1 imaginary frequency (Å)

	X	Y	Z
C	-0.83109200	-2.43696900	1.48295800
H	-1.16628600	-3.44135100	1.22312500
H	-1.17347500	-2.25044200	2.49979600
C	0.73390500	-2.41644100	1.50935600
H	1.10666600	-3.42589200	1.31846400
H	1.04254900	-2.14900800	2.51801600
C	1.87386300	-2.12182300	-0.67395500
H	2.46015800	-3.01565000	-0.43615100
H	2.52771900	-1.41316200	-1.18680100
C	0.71104500	-2.49020800	-1.58357100
H	0.08806300	-3.24742200	-1.10808900
H	1.09266400	-2.92440400	-2.50913000
C	-1.58105300	-1.57098900	-1.96062300
H	-2.06606300	-0.63357400	-2.23374400
H	-1.80181500	-2.30688500	-2.73974600
C	-2.11640400	-2.09885900	-0.62220700
H	-1.94877500	-3.17316300	-0.55591500
H	-3.19826100	-1.95196300	-0.60172600
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H	-3.43779000	-1.10202800	1.42110700
H	-2.07432500	-0.41205800	2.30748900
C	-2.61761000	0.71003900	0.60494500
C	-3.20835700	2.89849300	-0.29420300
H	-3.70131000	3.81436700	-0.57819800
C	-1.95108000	2.48336500	-0.58751800
H	-1.22596700	3.02590100	-1.17406800
C	2.52206300	-0.75264100	1.22936500
H	2.23573500	-0.52535900	2.25827100
H	3.43154000	-1.36049900	1.26088400
C	2.76613600	0.54242900	0.50788600
C	3.51480900	2.66053200	-0.44012600
H	4.07108700	3.53431200	-0.73969600
C	2.23224400	2.32836000	-0.72909300
H	1.54816600	2.90715300	-1.33036300
N	-1.49450700	-1.45523800	0.58138600
N	1.39903000	-1.46725800	0.57942000
N	-0.12751600	-1.29158100	-1.86921800
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N	-1.62574900	1.24583900	-0.07240000

N	1.81826800	1.12969900	-0.18692600
S	-4.02896600	1.69954400	0.65154700
S	4.24738500	1.42844500	0.53612700
Zn	0.04137800	0.03267500	-0.25357700

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Zero-point correction= 0.355585
Thermal correction to Energy= 0.374880
Thermal correction to Enthalpy= 0.375825
Thermal correction to Gibbs Free Energy= 0.308414
Sum of electronic and zero-point Energies= -3395.436236
Sum of electronic and thermal Energies= -3395.416941
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Sum of electronic and thermal Free Energies= -3395.483407

(δδλ)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies (Å)

	X	Y	Z
C	-0.97575300	-2.47421700	1.28571000
H	-0.82604100	-3.39029700	0.72001400
H	-1.63335100	-2.73493400	2.12046200
C	0.35339900	-1.98262100	1.85933200
H	0.86091100	-2.82137600	2.34895300
H	0.16587200	-1.21641800	2.61372800
C	1.76322300	-2.27433800	-0.21132500
H	2.11635700	-3.20483200	0.24524000
H	2.62731000	-1.76785500	-0.64476400
C	0.78063100	-2.60472600	-1.34393500
H	0.05120600	-3.34736300	-1.03159700
H	1.34821500	-3.05143600	-2.16203300
C	-1.39169600	-1.65029300	-2.12557100
H	-1.78843200	-0.71945900	-2.53292300
H	-1.51083300	-2.43038200	-2.88299400
C	-2.17023700	-2.06220100	-0.85681300
H	-2.18231100	-3.14852200	-0.75698600
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C	-2.59544400	-0.63547200	1.11798700
H	-3.59661600	-1.07826200	1.12366700
H	-2.27147100	-0.54590100	2.15852400
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C	-3.04084900	3.04502000	-0.17964600
H	-3.46086000	4.01604500	-0.38728500
C	-1.81083100	2.56738000	-0.48991000
H	-1.03437100	3.10639900	-1.01037800
C	2.33666200	-0.60731100	1.46445400
H	1.98409400	-0.19869300	2.41423600
H	3.19281600	-1.25324100	1.67951600

C	2.72877900	0.53264600	0.56567800
C	3.69893100	2.40745100	-0.65563000
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C	2.41726300	2.11232400	-0.98768300
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N	-1.62030200	-1.47024600	0.39630300
N	1.22312400	-1.35429600	0.83380200
N	0.04397900	-1.40051500	-1.82968700
H	0.48918000	-1.05080000	-2.67422700
N	-1.58635100	1.26678700	-0.08604200
N	1.87808400	1.05270600	-0.29009100
S	-3.96513000	1.82847500	0.64020300
S	4.26715700	1.31642000	0.56677600
Zn	0.04380800	0.03641200	-0.32913900

E(RTPSSh) = -3395.7970602 Hartree

Zero-point correction=	0.356084
Thermal correction to Energy=	0.375888
Thermal correction to Enthalpy=	0.376832
Thermal correction to Gibbs Free Energy=	0.308337
Sum of electronic and zero-point Energies=	-3395.440976
Sum of electronic and thermal Energies=	-3395.421172
Sum of electronic and thermal Enthalpies=	-3395.420228
Sum of electronic and thermal Free Energies=	-3395.488723

TS2-(δXλ)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 1 imaginary frequency (Å)

	X	Y	Z
C	0.94008800	2.46071200	1.27717900
H	0.82491600	3.34898400	0.66139800
H	1.59414900	2.74778900	2.10628200
C	-0.40813900	2.01605500	1.85479000
H	-0.91515100	2.88551400	2.28731400
H	-0.23834900	1.29868000	2.65905100
C	-1.90978900	2.22283400	-0.15166300
H	-2.37999200	3.08217900	0.33862500
H	-2.70042200	1.63476300	-0.62158000
C	-0.95518800	2.71935400	-1.23763100
H	-0.32822100	3.52769600	-0.86928400
H	-1.55185800	3.13394300	-2.05201400
C	1.33179400	2.09687700	-2.00226600
H	1.73332800	1.48272500	-2.80716700
H	1.32699300	3.13276000	-2.34715800
C	2.25945600	1.94758300	-0.75586700
H	2.73065500	2.90435400	-0.51645500
H	3.05695800	1.25034300	-1.01187300
C	2.47474100	0.53750800	1.23071200

H	3.46780700	0.97942800	1.36038800
H	2.04327000	0.39757400	2.22516700
C	2.56498700	-0.80105200	0.55144700
C	3.05431400	-3.02288400	-0.32759400
H	3.49557100	-3.97281100	-0.58333700
C	1.85808400	-2.51043700	-0.70938600
H	1.13956500	-2.99211600	-1.35443000
C	-2.29900800	0.49095900	1.49961300
H	-1.87987000	0.06892100	2.41571100
H	-3.18816100	1.06604600	1.77443200
C	-2.65199900	-0.63541100	0.56722800
C	-3.55395500	-2.51271500	-0.70183300
H	-4.16067800	-3.30685700	-1.10661000
C	-2.30740600	-2.12266700	-1.06776300
H	-1.71063500	-2.56119400	-1.85301800
N	1.57489800	1.40502700	0.44657500
N	-1.26666000	1.33335100	0.85496900
N	-0.06431500	1.63766700	-1.76592000
H	-0.43892800	1.32028700	-2.65530200
N	1.59055600	-1.25421800	-0.20780100
N	-1.80631400	-1.06198500	-0.34357300
S	3.88981600	-1.89616800	0.69189200
S	-4.13834300	-1.51294400	0.58935800
Zn	-0.01765200	0.04592000	-0.38672400

E(RTPSSh) =-3395.7960333 Hartree

Zero-point correction=	0.356194
Thermal correction to Energy=	0.375291
Thermal correction to Enthalpy=	0.376235
Thermal correction to Gibbs Free Energy=	0.309786
Sum of electronic and zero-point Energies=	-3395.439839
Sum of electronic and thermal Energies=	-3395.420743
Sum of electronic and thermal Enthalpies=	-3395.419798
Sum of electronic and thermal Free Energies=	-3395.486247

(δλλ)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies (Å)

	X	Y	Z
C	-0.99725500	2.42219100	-1.28472300
H	-0.85105900	3.30534200	-0.66721800
H	-1.67116600	2.72303300	-2.09255200
C	0.32968800	1.95866700	-1.90410500
H	0.82402000	2.81639300	-2.37255700
H	0.12314900	1.22917500	-2.68851300
C	1.97893900	2.19000800	-0.01743700
H	2.49322500	2.97241700	-0.58659600
H	2.74007700	1.57275300	0.46226000

C	1.11663000	2.84189500	1.06334600
H	0.58996200	3.70604700	0.66413300
H	1.77963300	3.21462700	1.84554600
C	-1.25945000	2.51689200	1.76773600
H	-1.63585700	2.36459900	2.77871200
H	-1.17990400	3.59387400	1.61463800
C	-2.26929700	1.89697000	0.78048900
H	-3.03981300	2.63520100	0.53287200
H	-2.76256700	1.04637300	1.25418900
C	-2.50400900	0.46714600	-1.18107600
H	-3.51780100	0.87070200	-1.27146400
H	-2.10967000	0.33883500	-2.19206700
C	-2.52041700	-0.87262700	-0.49507400
C	-2.88134800	-3.12253400	0.37721300
H	-3.26284300	-4.10101100	0.62125800
C	-1.73574900	-2.52758100	0.79231900
H	-1.00299500	-2.95745900	1.45770000
C	2.16356800	0.34960700	-1.57788400
H	1.65642200	-0.12185600	-2.42240300
H	3.05416400	0.85532300	-1.96369900
C	2.54311400	-0.71381200	-0.58246400
C	3.47982600	-2.50255600	0.78634500
H	4.08991700	-3.28012200	1.21740100
C	2.27957700	-2.03070900	1.20702600
H	1.73385200	-2.36929500	2.07475800
N	-1.61164700	1.37318600	-0.43804700
N	1.22428300	1.28913100	-0.92759100
N	0.10634900	1.90926500	1.66439500
H	0.41511300	1.67046600	2.60132000
N	-1.54157900	-1.25645900	0.29452700
N	1.75831800	-1.02192000	0.42565100
S	-3.76221400	-2.05805500	-0.67114500
S	3.99262800	-1.64984100	-0.63422500
Zn	-0.00151400	0.13157300	0.48318000

E(RTPSSh) =-3395.7971541 Hartree
Zero-point correction= 0.355572
Thermal correction to Energy= 0.375620
Thermal correction to Enthalpy= 0.376564
Thermal correction to Gibbs Free Energy= 0.307379
Sum of electronic and zero-point Energies= -3395.441582
Sum of electronic and thermal Energies= -3395.421534
Sum of electronic and thermal Enthalpies= -3395.420590
Sum of electronic and thermal Free Energies= -3395.489775

TS3-(Xλλ)-[Zn(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 1 imaginary frequency (Å)

	X	Y	Z
C	-0.96100200	2.44227600	-1.23638600
H	-0.64770800	3.27018000	-0.60051800
H	-1.65896800	2.85620200	-1.97023100
C	0.25052100	1.85148400	-1.95370200
H	0.74531600	2.63341300	-2.53971100
H	-0.07039600	1.06790700	-2.64254200
C	1.96375600	2.21418400	-0.17721300
H	2.10018200	3.12914000	-0.76012900
H	2.95142300	1.78176900	-0.02443100
C	1.38701500	2.57924400	1.22459200
H	1.11118100	3.63365400	1.24030700
H	2.18723700	2.44821500	1.95149000
C	-1.06576600	2.54877300	1.76779600
H	-1.42132100	2.55856400	2.79798800
H	-0.86042800	3.58343600	1.49213500
C	-2.16691700	1.96074100	0.87971900
H	-2.93042400	2.72452700	0.69178300
H	-2.64916300	1.12498500	1.39132300
C	-2.58649700	0.58611800	-1.09183600
H	-3.58635900	1.03247200	-1.09924000
H	-2.26727800	0.48013200	-2.13147400
C	-2.61561000	-0.77883400	-0.45702700
C	-3.02371700	-3.04621900	0.34780100
H	-3.43475100	-4.01557000	0.57990100
C	-1.82363400	-2.52398900	0.70170500
H	-1.06747300	-3.01645700	1.29350600
C	2.10673800	0.27090700	-1.64093100
H	1.55843100	-0.24903500	-2.43006800
H	2.96751900	0.76399800	-2.10179000
C	2.54518500	-0.73561300	-0.61227900
C	3.55186100	-2.45202000	0.79773900
H	4.19064300	-3.19742400	1.24379100
C	2.34391100	-2.00199000	1.22116500
H	1.81761600	-2.32988000	2.10491700
N	-1.60941400	1.42376100	-0.37934600
N	1.18924600	1.23153800	-0.98736600
N	0.21684200	1.77336500	1.69550400
H	0.43335300	1.44875500	2.63224500
N	-1.60249800	-1.24229700	0.24244100
N	1.78380300	-1.03283900	0.41740000
S	-3.92331500	-1.89656000	-0.58869700
S	4.01981900	-1.63084800	-0.65647000
Zn	-0.00978700	0.07148300	0.44187100

E(RTPSSh) = -3395.7944702 Hartree

Zero-point correction=	0.355739
Thermal correction to Energy=	0.374976
Thermal correction to Enthalpy=	0.375921
Thermal correction to Gibbs Free Energy=	0.308822
Sum of electronic and zero-point Energies=	-3395.438732

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 Sum of electronic and thermal Energies=             -
3395.419494
 Sum of electronic and thermal Enthalpies=           -
3395.418550
 Sum of electronic and thermal Free Energies=        -
3395.485648
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N5-[Cu(no2th)]$^{+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies (Å)

	X	Y	Z
C	-0.33111000	-1.99528000	-1.87471500
H	-0.81372700	-2.80864100	-2.43837600
H	-0.04529000	-1.22146900	-2.59104300
C	0.93202000	-2.55215800	-1.20431000
H	0.68209900	-3.42229300	-0.59589600
H	1.60380300	-2.91956000	-1.99001500
C	1.95753300	-2.02195600	0.99146600
H	2.64726100	-2.88064100	0.96012000
H	2.48264600	-1.19732600	1.48080800
C	0.73944200	-2.40145700	1.83681100
H	0.29488200	-3.32887200	1.46977800
H	1.08027000	-2.60642800	2.85472600
C	-1.66585300	-1.83717200	1.54045200
H	-2.35457000	-1.01378500	1.73345100
H	-1.94915600	-2.67272900	2.19471300
C	-1.79796400	-2.31249600	0.08705400
H	-1.28871000	-3.27019100	-0.02917200
H	-2.85872600	-2.50719500	-0.11170700
C	-2.26622600	-0.53390300	-1.53952600
H	-3.16901900	-1.09873800	-1.80887000
H	-1.84968300	-0.12809300	-2.46647600
C	-2.62616800	0.62693700	-0.65046200
C	-3.59634900	2.54418600	0.51283400
H	-4.23083200	3.32901300	0.89335800
C	-2.30666100	2.26163300	0.82943200
H	-1.70077500	2.80576800	1.53914500
C	2.65171100	-0.81422500	-1.01126600
H	2.40571800	-0.73408900	-2.07428900
H	3.62919600	-1.31466600	-0.94572300
C	2.75381900	0.57966800	-0.44911700
C	3.35921000	2.85242000	0.21880700
H	3.84923700	3.79390100	0.41036300
C	2.09435900	2.47323000	0.52814600
H	1.36030900	3.08507600	1.03137100
N	-1.24534700	-1.36799900	-0.90608400
N	1.58807200	-1.55770400	-0.34941400
N	-0.30468700	-1.33954300	1.84956600
H	-0.33295500	-0.92536600	2.77602700
N	-1.76167500	1.17970700	0.16678900
N	1.75470600	1.18701800	0.14947000
S	-4.18165000	1.40730700	-0.65909000

S	4.19053700	1.55387300	-0.57689000
Cu	0.02799200	0.19760500	0.42129200

E(RTPSSh) = -3257.0639442 Hartree
Zero-point correction= 0.352109
Thermal correction to Energy= 0.372698
Thermal correction to Enthalpy= 0.373642
Thermal correction to Gibbs Free Energy= 0.302978
Sum of electronic and zero-point Energies= -3256.711835
Sum of electronic and thermal Energies= -3256.691246
Sum of electronic and thermal Enthalpies= -3256.690302
Sum of electronic and thermal Free Energies= -3256.760966

N3S2-[Cu(no2th)]$^{+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies (Å)

	X	Y	Z
C	-0.08287700	-1.91232800	-1.81863200
H	-0.59293000	-2.74811900	-2.31550200
H	0.18082300	-1.18001000	-2.58467000
C	1.18893200	-2.44055700	-1.14439300
H	0.95627300	-3.29226100	-0.50467800
H	1.86259900	-2.81675500	-1.92054500
C	2.22770000	-1.84953400	1.03994400
H	2.89344000	-2.72266500	1.00571700
H	2.77951900	-1.02626800	1.49916000
C	1.00745300	-2.18298800	1.90377300
H	0.55468300	-3.12083100	1.57863800
H	1.34291200	-2.33828900	2.93107200
C	-1.40516900	-1.62943700	1.59634900
H	-2.09140500	-0.79811200	1.76092300
H	-1.67282700	-2.43433100	2.29113500
C	-1.54576600	-2.15934700	0.16556900
H	-1.03137400	-3.11561500	0.06832900
H	-2.60328100	-2.35527700	-0.02971400
C	-2.09093800	-0.55527700	-1.62167100
H	-2.75788400	-1.29258600	-2.08326400
H	-1.62499500	0.03474300	-2.41309900
C	-2.92984300	0.32056000	-0.74396600
C	-3.81493900	2.02837000	0.76376100
H	-3.98121200	2.87218500	1.41524300
C	-4.68643900	1.05411500	0.38384800
H	-5.71859200	0.98909300	0.69989000
C	2.93348200	-0.66945200	-0.99584500
H	2.73601600	-0.67989600	-2.06933200
H	3.91447800	-1.12336500	-0.82121900
C	2.96465500	0.74751600	-0.49641400
C	2.30920300	2.99826000	0.25792300

H	1.82809400	3.94178300	0.46249600
C	3.55661800	2.58399800	0.58949900
H	4.27042600	3.16722800	1.15496600
N	-0.99838100	-1.22129600	-0.86501000
N	1.84385800	-1.40360000	-0.31707000
N	-0.03618300	-1.11457000	1.85777400
H	-0.04572600	-0.61856800	2.74316100
N	-4.18210500	0.09338600	-0.46356800
N	3.91197900	1.30965900	0.17766300
S	-2.26925600	1.75771200	0.02641700
S	1.51012100	1.77620800	-0.70440000
Cu	0.32346600	0.08506100	0.20593300

E(RTPSSh) = -3257.0442159 Hartree
Zero-point correction= 0.352622
Thermal correction to Energy= 0.373141
Thermal correction to Enthalpy= 0.374085
Thermal correction to Gibbs Free Energy= 0.303031
Sum of electronic and zero-point Energies= -3256.691594
Sum of electronic and thermal Energies= -3256.671075
Sum of electronic and thermal Enthalpies= -3256.670131
Sum of electronic and thermal Free Energies= -3256.741184

N5-[Cu(no2th)]$^{2+}$, TPSSh/TZVP, Aqueous solution, 0 imaginary frequencies (Å)

	X	Y	Z
C	-0.40662400	-2.01599900	-1.86508700
H	-0.92905200	-2.83094400	-2.37664800
H	-0.12929400	-1.26797700	-2.60883700
C	0.83668200	-2.55200700	-1.16679900
H	0.59439600	-3.40396100	-0.53439300
H	1.55781200	-2.90430300	-1.90693300
C	1.86889700	-2.00757600	1.04017100
H	2.54883200	-2.85729500	0.92245900
H	2.41230900	-1.19745900	1.52954100
C	0.65740900	-2.40054000	1.88332000
H	0.21964100	-3.33368200	1.52651300
H	0.99183800	-2.58443600	2.90569400
C	-1.75049500	-1.81520900	1.57283700
H	-2.42807900	-0.98484500	1.77146000
H	-2.03620800	-2.64541600	2.22788300
C	-1.88507000	-2.29005800	0.12160700
H	-1.38789300	-3.25104200	-0.00304000
H	-2.94035000	-2.45129200	-0.10783900
C	-2.31045300	-0.46614200	-1.50968400
H	-3.24152600	-1.00555000	-1.69879100
H	-1.92037100	-0.12408600	-2.47145300

C	-2.52884000	0.72534100	-0.62466500
C	-3.19218900	2.70528400	0.63054300
H	-3.71353000	3.54765000	1.05608400
C	-1.93719300	2.26318000	0.89393600
H	-1.25041900	2.69648800	1.60414600
C	2.59010900	-0.81078500	-0.98109800
H	2.36809900	-0.75110300	-2.04917100
H	3.51642800	-1.37820200	-0.85976700
C	2.70178600	0.57623400	-0.42763900
C	3.20301700	2.84727100	0.28812000
H	3.66542600	3.79439300	0.51538700
C	1.92286400	2.45473900	0.50469900
H	1.14820800	3.05482000	0.95473800
N	-1.29238000	-1.33853200	-0.87302700
N	1.45557800	-1.49408700	-0.30249200
N	-0.37947000	-1.33579800	1.84861200
H	-0.37752600	-0.82202100	2.72395900
N	-1.56806600	1.14768800	0.17339300
N	1.64736900	1.16759300	0.09567100
S	-3.95634300	1.68745900	-0.54657300
S	4.11229600	1.56611100	-0.44502700
Cu	0.04053100	-0.05749300	0.13751500

E(UTPSSh) = -3256.9155984 Hartree
Zero-point correction = 0.356055
Thermal correction to Energy = 0.375618
Thermal correction to Enthalpy = 0.376563
Thermal correction to Gibbs Free Energy = 0.308398
Sum of electronic and zero-point Energies = -3256.559543
Sum of electronic and thermal Energies = -3256.539980
Sum of electronic and thermal Enthalpies = -3256.539036
Sum of electronic and thermal Free Energies = -3256.607200