Supporting Information for:

$[Tl^{III}(dota)]^{-}$: An extraordinary robust macrocyclic complex

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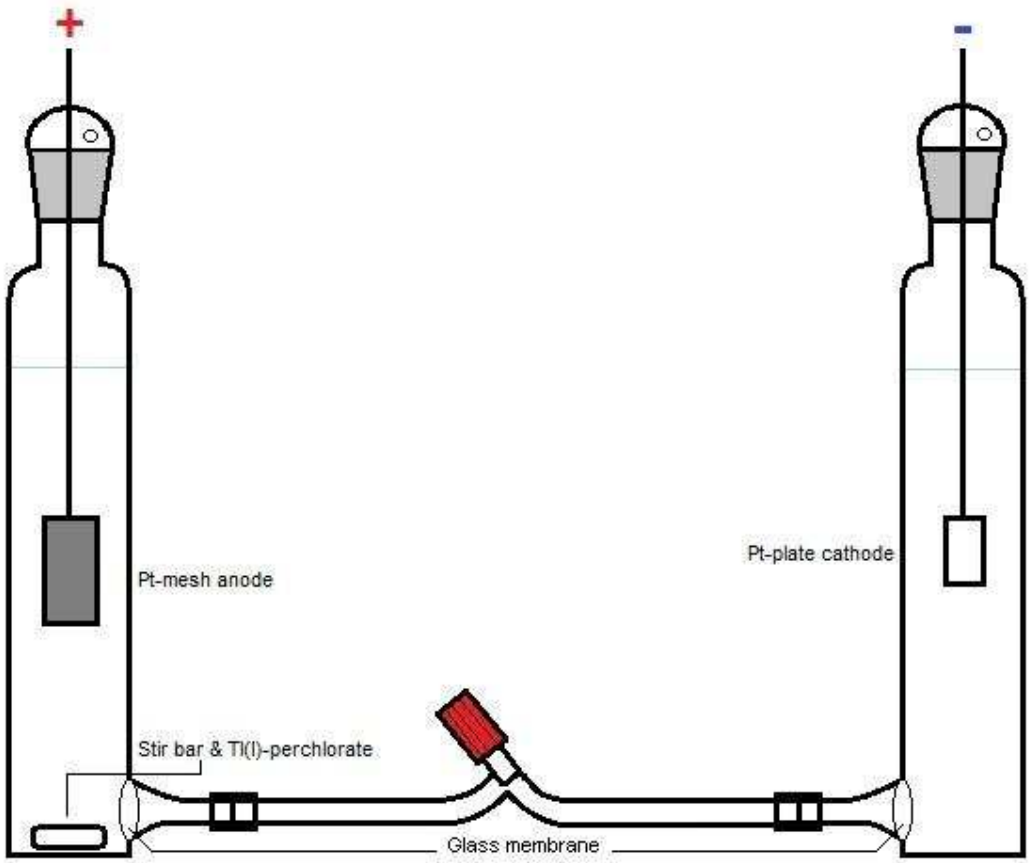

Figure S1: Scheme of the $Tl(ClO_4)_3$ electrolysis device.

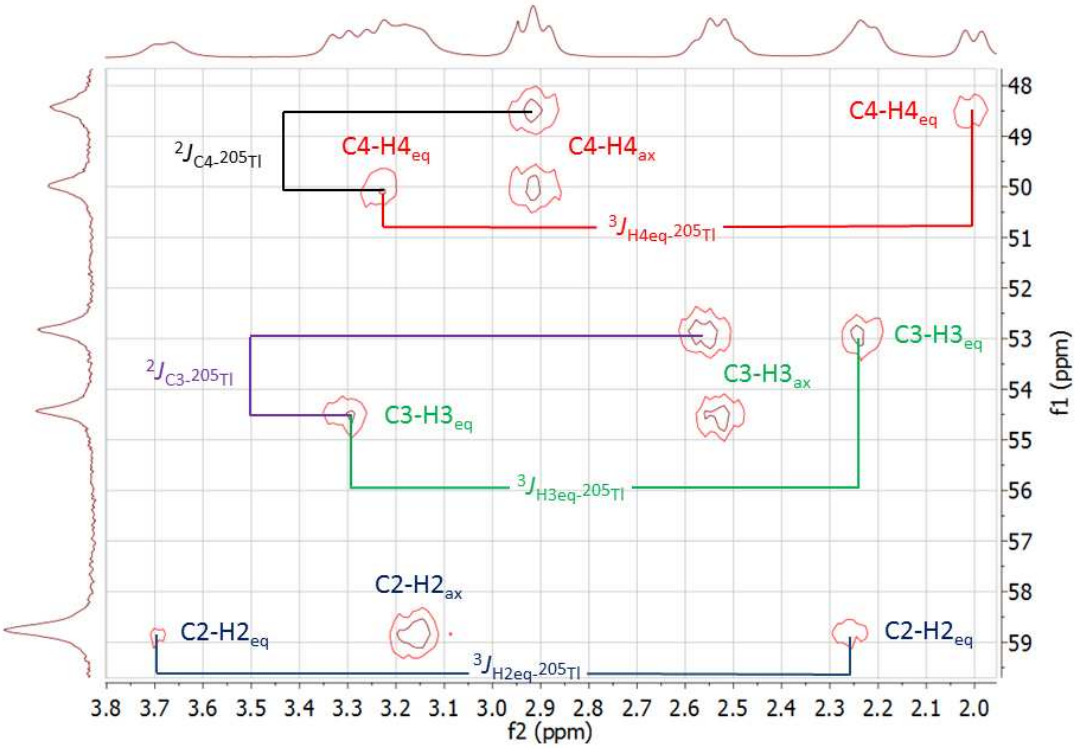

Figure S2: 400MHz ^{1}H-^{13}C HSQC spectrum of 0.1 M [Tl(dota)]$^{-}$ at 272.5 K

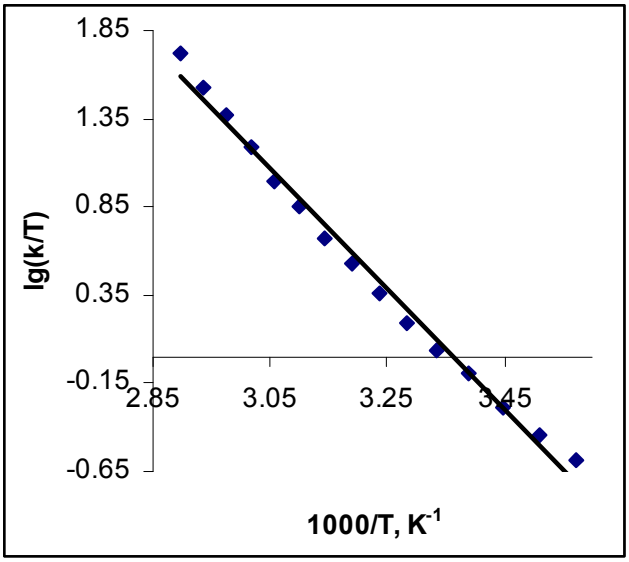

Figure S3: Modified Eyring diagram of the reaction rates obtained for [Tl(dota]$^{-}$.

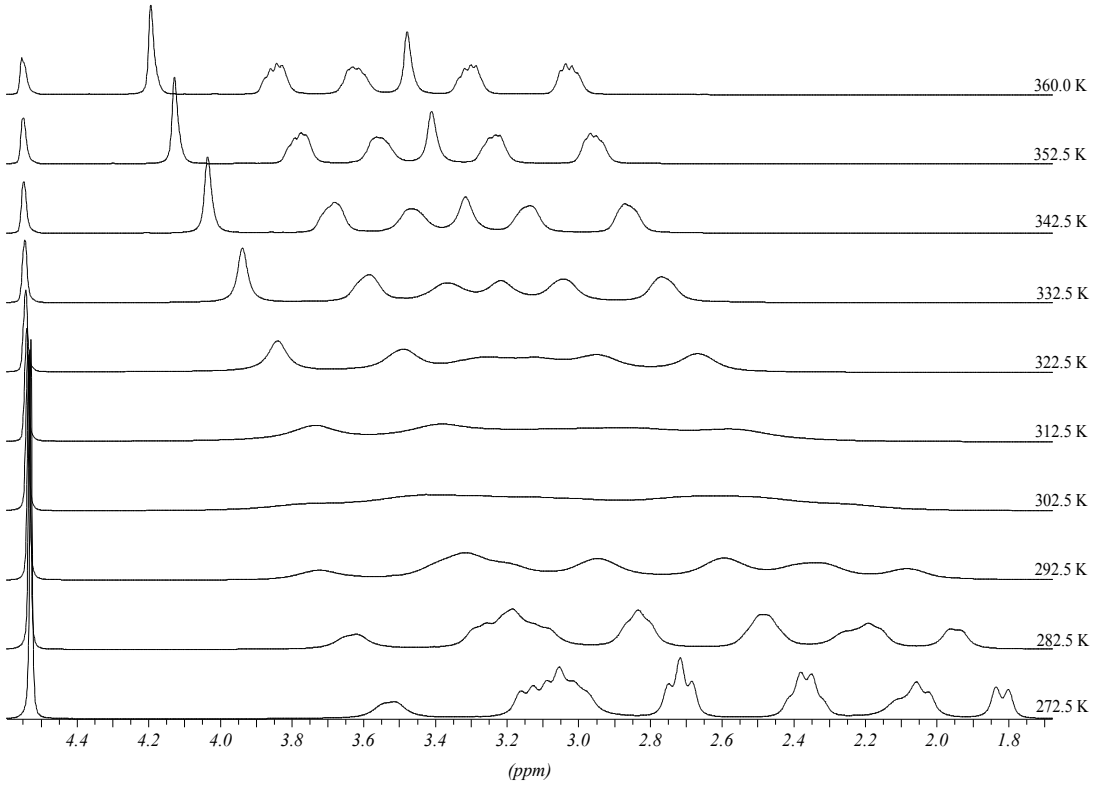

Figure S4: ^{1}H-NMR spectra of 0.1 M [Tl(dota)]$^{-}$ at varying temperatures.

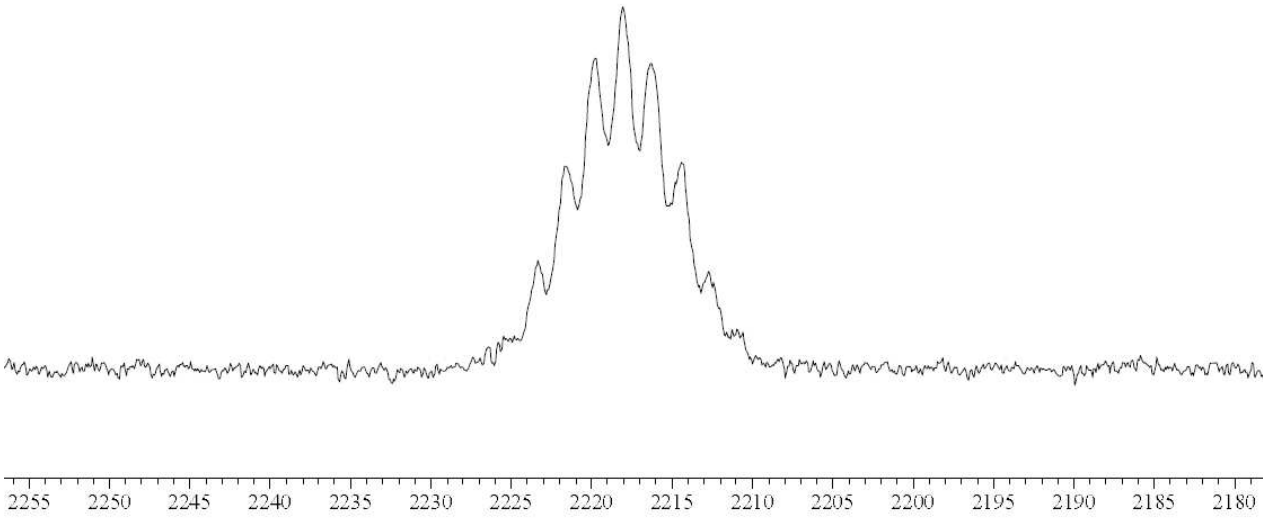

Figure S5: 288.5 MHz ^{205}Tl-NMR spectrum of [Tl(dota)]$^{-}$ at 268 K

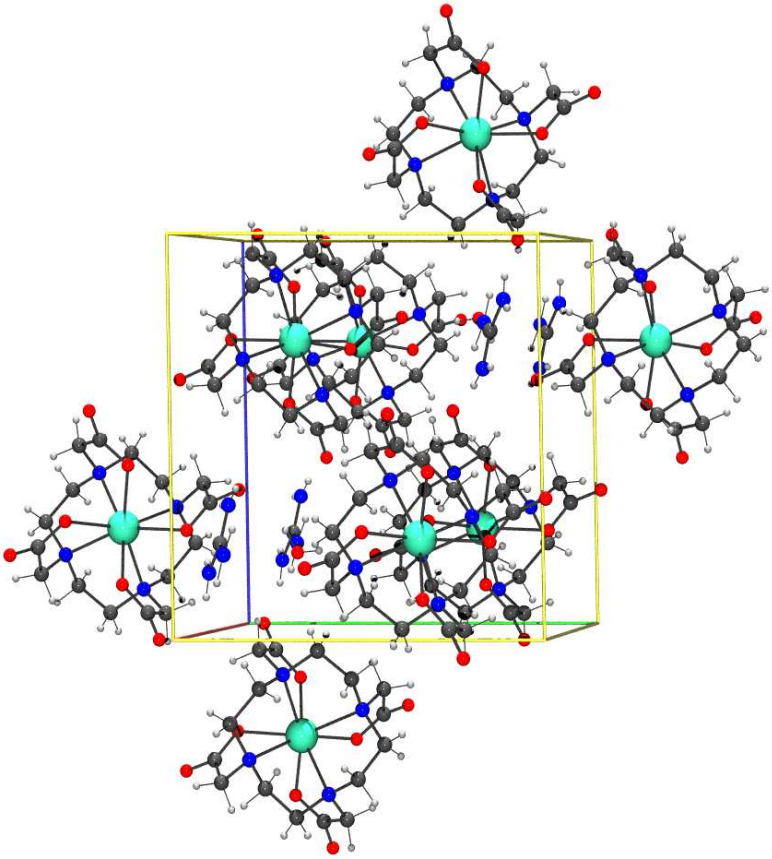

Figure S6: Packing diagram of $\{C(NH_2)_3\}[Tl(dota)]\cdot H_2O$, view normal to (100).

Table S1: Cartesian coordinates of the Intermediates and the Transition States of the $[Tl(dota)]^-$ system optimized at B3LYP/CRENBL/6-31+G(d,p) level using Polarizable Continuum Model (water solvent).

TSAP'

N	0.19867600	2.10388700	-1.10374600
C	-0.83510600	2.10364600	-2.16241800
C	-2.18135300	1.56573600	-1.67534800
N	-2.10388700	0.19867600	-1.10374600
C	-2.10364600	-0.83510600	-2.16241800
C	-1.56573600	-2.18135300	-1.67534800
N	-0.19867600	-2.10388700	-1.10374600
C	0.83510600	-2.10364600	-2.16241800
C	2.18135300	-1.56573600	-1.67534800
N	2.10388700	-0.19867600	-1.10374600

C	2.10364600	0.83510600	-2.16241800
C	1.56573600	2.18135300	-1.67534800
C	0.00000000	3.18915900	-0.12090100
C	0.73156900	2.93984500	1.21180700
O	1.06132900	1.73250700	1.49062100
O	0.94428800	3.93047700	1.93777300
C	-3.18915900	0.00000000	-0.12090100
C	-2.93984500	0.73156900	1.21180700
O	-1.73250700	1.06132900	1.49062100
O	-3.93047700	0.94428800	1.93777300
C	0.00000000	-3.18915900	-0.12090100
C	-0.73156900	-2.93984500	1.21180700
O	-1.06132900	-1.73250700	1.49062100
O	-0.94428800	-3.93047700	1.93777300
C	3.18915900	0.00000000	-0.12090100
C	2.93984500	-0.73156900	1.21180700
O	1.73250700	-1.06132900	1.49062100
O	3.93047700	-0.94428800	1.93777300
H	-0.46541600	1.50332300	-2.99658000
H	-0.98829100	3.11979700	-2.55310600
H	-2.58447100	2.22737000	-0.90663800
H	-2.89231900	1.58860900	-2.51274400
H	-1.50332300	-0.46541600	-2.99658000
H	-3.11979700	-0.98829100	-2.55310600
H	-2.22737000	-2.58447100	-0.90663800
H	-1.58860900	-2.89231900	-2.51274400
H	0.46541600	-1.50332300	-2.99658000
H	0.98829100	-3.11979700	-2.55310600
H	2.58447100	-2.22737000	-0.90663800
H	2.89231900	-1.58860900	-2.51274400
H	1.50332300	0.46541600	-2.99658000
H	3.11979700	0.98829100	-2.55310600
H	2.22737000	2.58447100	-0.90663800
H	1.58860900	2.89231900	-2.51274400
H	0.32525400	4.15387100	-0.53108300
H	-1.06227500	3.27159900	0.11764800
H	-4.15387100	0.32525400	-0.53108300
H	-3.27159900	-1.06227500	0.11764800
H	-0.32525400	-4.15387100	-0.53108300
H	1.06227500	-3.27159900	0.11764800
H	4.15387100	-0.32525400	-0.53108300
H	3.27159900	1.06227500	0.11764800
Tl	0.00000000	0.00000000	0.30433200

Sum of electronic and zero-point Energies= -1496.446962
Sum of electronic and thermal Energies= -1496.420375
Sum of electronic and thermal Enthalpies= -1496.419431
Sum of electronic and thermal Free Energies= -1496.500070

SAP'

N	0.22895800	2.12231900	-1.02933400
C	1.59561300	2.16468500	-1.60955800
C	2.09001400	0.80068600	-2.09556300
N	2.12231900	-0.22895800	-1.02933400

C	2.16468500	-1.59561300	-1.60955800
C	0.80068600	-2.09001400	-2.09556300
N	-0.22895800	-2.12231900	-1.02933400
C	-1.59561300	-2.16468500	-1.60955800
C	-2.09001400	-0.80068600	-2.09556300
N	-2.12231900	0.22895800	-1.02933400
C	-2.16468500	1.59561300	-1.60955800
C	-0.80068600	2.09001400	-2.09556300
C	0.00000000	3.23688900	-0.07958300
C	-0.90772100	2.93499400	1.12989500
O	-1.11946300	1.71517900	1.45336200
O	-1.35689700	3.92614700	1.74082000
C	3.23688900	0.00000000	-0.07958300
C	2.93499400	0.90772100	1.12989500
O	3.92614700	1.35689700	1.74082000
O	1.71517900	1.11946300	1.45336200
C	0.00000000	-3.23688900	-0.07958300
C	0.90772100	-2.93499400	1.12989500
O	1.35689700	-3.92614700	1.74082000
O	1.11946300	-1.71517900	1.45336200
C	-3.23688900	0.00000000	-0.07958300
C	-2.93499400	-0.90772100	1.12989500
O	-3.92614700	-1.35689700	1.74082000
O	-1.71517900	-1.11946300	1.45336200
H	0.96084500	3.53031200	0.34880600
H	-0.40644100	4.11248100	-0.60064400
H	4.11248100	0.40644100	-0.60064400
H	3.53031200	-0.96084500	0.34880600
H	0.40644100	-4.11248100	-0.60064400
H	-0.96084500	-3.53031200	0.34880600
H	-3.53031200	0.96084500	0.34880600
H	-4.11248100	-0.40644100	-0.60064400
H	2.27351500	2.54918600	-0.84691300
H	1.63569900	2.86626800	-2.45420200
H	3.09481900	0.93435000	-2.52132200
H	1.45819100	0.43413700	-2.90700400
H	2.86626800	-1.63569900	-2.45420200
H	2.54918600	-2.27351500	-0.84691300
H	0.93435000	-3.09481900	-2.52132200
H	0.43413700	-1.45819100	-2.90700400
H	-1.63569900	-2.86626800	-2.45420200
H	-2.27351500	-2.54918600	-0.84691300
H	-1.45819100	-0.43413700	-2.90700400
H	-3.09481900	-0.93435000	-2.52132200
H	-2.54918600	2.27351500	-0.84691300
H	-2.86626800	1.63569900	-2.45420200
H	-0.43413700	1.45819100	-2.90700400
H	-0.93435000	3.09481900	-2.52132200
Tl	0.00000000	0.00000000	0.32405000

Sum of electronic and zero-point Energies= -1496.443408
Sum of electronic and thermal Energies= -1496.416732
Sum of electronic and thermal Enthalpies= -1496.415788
Sum of electronic and thermal Free Energies= -1496.496765

I1

N	0.78141000	1.90047900	1.19785000
C	-0.27182000	2.21762200	2.19402400
C	-1.68547500	2.08306900	1.63875200
N	-1.99370600	0.76362200	1.03063200
C	-2.30239300	-0.30338300	2.01837300
C	-1.10564200	-1.18223600	2.41541800
N	-0.45303600	-1.86308700	1.26874900
C	0.84164200	-2.48751700	1.65278100
C	1.97001900	-1.48757900	1.89165600
N	2.25910500	-0.63710200	0.71437400
C	2.95678200	0.60954200	1.11097000
C	2.05972100	1.57814700	1.88163400
C	0.95737800	2.99360300	0.21278100
C	1.61028600	2.57952200	-1.12215600
O	1.50230900	1.35694100	-1.49519200
O	2.18391600	3.47658900	-1.76915200
C	-3.07749100	0.95759300	0.03923500
C	-2.58649000	1.56383300	-1.28903400
O	-3.45040700	2.07268800	-2.03028800
O	-1.33311700	1.49867900	-1.55499500
C	-1.34886600	-2.86582000	0.63935600
C	-2.07308300	-2.43687100	-0.65139700
O	-2.93302100	-3.23538600	-1.08073600
O	-1.75221200	-1.33165700	-1.19924300
C	3.02341500	-1.36547300	-0.32327300
C	2.21055500	-2.01400400	-1.45845600
O	2.80727700	-2.86400000	-2.14935900
O	1.00615000	-1.62650800	-1.65660600
H	-0.02440300	3.39399400	-0.05196100
H	1.54311600	3.81210000	0.64912800
H	-3.86754900	1.60183300	0.44537300
H	-3.52354300	-0.00601400	-0.20550600
H	-2.10549700	-3.20720000	1.35507800
H	-0.76208700	-3.74724000	0.37022600
H	3.69623100	-0.66081400	-0.81942000
H	3.65376800	-2.14065800	0.12878600
H	-0.15004000	3.24022700	2.57871700
H	-0.14220500	1.54874200	3.04660600
H	-1.84588200	2.84078600	0.86908100
H	-2.39643400	2.30162000	2.44772200
H	-2.71386400	0.13211400	2.93806200
H	-3.08644200	-0.93652200	1.59826100
H	-1.46413400	-1.92791200	3.13985100
H	-0.35386800	-0.58297400	2.93018300
H	0.71795000	-3.09477500	2.56027700
H	1.12525700	-3.16646600	0.84679100
H	1.72543600	-0.84448800	2.73732500
H	2.86616900	-2.05293000	2.18507900
H	3.32682000	1.08123400	0.20215100
H	3.82839500	0.38345300	1.74304000
H	1.82039200	1.16281400	2.86180000
H	2.63256300	2.49629000	2.07045200
Tl	0.00030900	-0.00239100	-0.34231800

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Sum of electronic and zero-point Energies=          -1496.435709
Sum of electronic and thermal Energies=             -1496.408903
Sum of electronic and thermal Enthalpies=           -1496.407959
Sum of electronic and thermal Free Energies=        -1496.491449
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I2a

N	-0.71087800	1.67201200	-1.44083600
C	0.46456100	2.11742800	-2.23482700
C	1.74663500	2.19214200	-1.40367600
N	2.10666900	0.93816800	-0.69725900
C	2.71443100	-0.10171200	-1.56661900
C	1.71618900	-1.00345300	-2.30602200
N	0.71088200	-1.67201400	-1.44083200
C	-0.46455500	-2.11742900	-2.23482700
C	-1.74663100	-2.19214300	-1.40367900
N	-2.10666700	-0.93816900	-0.69726400
C	-2.71442700	0.10171000	-1.56662600
C	-1.71618300	1.00345000	-2.30602800
C	-1.29201800	2.81113100	-0.68990600
C	-2.02384000	2.45950100	0.61831000
O	-1.75456900	1.34143100	1.17355400
O	-2.81366900	3.31804900	1.06221100
C	2.98423600	1.26572000	0.45010200
C	2.23530100	1.78728300	1.68872900
O	2.89789200	2.44303800	2.51636100
O	0.99368600	1.48881400	1.81477400
C	1.29201900	-2.81113200	-0.68990000
C	2.02383300	-2.45950300	0.61832100
O	2.81366600	-3.31804800	1.06222100
O	1.75456600	-1.34143000	1.17355900
C	-2.98423700	-1.26571900	0.45009600
C	-2.23530500	-1.78728200	1.68872500
O	-2.89789900	-2.44303500	2.51635600
O	-0.99369000	-1.48881300	1.81477300
H	-0.48347800	3.48976500	-0.40322400
H	-1.97516400	3.38073300	-1.33225200
H	3.74675400	2.00095300	0.16529500
H	3.49395700	0.35693200	0.77313700
H	1.97516900	-3.38073300	-1.33224200
H	0.48347800	-3.48976700	-0.40322300
H	-3.49395800	-0.35693100	0.77312800
H	-3.74675400	-2.00095300	0.16528700
H	0.28113300	3.10894000	-2.66970500
H	0.59358400	1.43786700	-3.07596300
H	1.63554600	2.96896700	-0.64262300
H	2.56827700	2.50825200	-2.06218600
H	3.35911800	0.36252200	-2.32587100
H	3.36030200	-0.71885000	-0.94158000
H	2.30003300	-1.75536200	-2.85596300
H	1.17507100	-0.42782000	-3.05528500
H	-0.59357600	-1.43786700	-3.07596300
H	-0.28112700	-3.10894100	-2.66970500
H	-2.56827200	-2.50825300	-2.06219000
H	-1.63554400	-2.96896800	-0.64262500

H	-3.36029900	0.71885000	-0.94159000
H	-3.35911200	-0.36252500	-2.32587900
H	-1.17506300	0.42781600	-3.05528900
H	-2.30002500	1.75535800	-2.85597200
Tl	0.00000000	0.00000000	0.33385600

Sum of electronic and zero-point Energies= -1496.437423
Sum of electronic and thermal Energies= -1496.410637
Sum of electronic and thermal Enthalpies= -1496.409693
Sum of electronic and thermal Free Energies= -1496.492679

I2b

N	2.08534700	-0.77144000	1.02170400
C	2.45357600	0.25066900	2.03026200
C	2.20247500	1.67689300	1.55182600
N	0.80644900	1.91674200	1.11022000
C	-0.11336000	2.07716900	2.25886000
C	-1.58516900	1.91915900	1.87524800
N	-1.92175700	0.61877300	1.23722700
C	-2.18758800	-0.47222500	2.21496900
C	-1.06247200	-1.51192100	2.32431800
N	-0.61438600	-2.03328200	1.01355300
C	0.62444600	-2.84515700	1.10269800
C	1.83595200	-2.09176700	1.65795800
C	3.09890300	-0.86620100	-0.05131700
C	2.59092400	-1.51460900	-1.35089100
O	1.33570300	-1.43743600	-1.60214900
O	3.43815600	-2.04986100	-2.09182400
C	0.78467900	3.06222400	0.17693900
C	1.34971700	2.70391700	-1.21275600
O	1.71958900	3.64835700	-1.93653200
O	1.39784500	1.46195800	-1.53290500
C	-3.05727700	0.80957300	0.30395500
C	-2.67744500	1.56245000	-0.98353400
O	-3.60581700	2.09186500	-1.62597300
O	-1.44077800	1.58003600	-1.31610500
C	-1.65946700	-2.80833600	0.30340900
C	-1.91409100	-2.41236800	-1.16632300
O	-2.56750300	-3.22824000	-1.84789400
O	-1.51004100	-1.26949200	-1.57155700
H	3.41665700	0.14250600	-0.32756100
H	3.98405700	-1.41267900	0.29756100
H	1.35375700	3.90793700	0.58378600
H	-0.24300200	3.39352600	0.02259100
H	-3.88384500	1.34038500	0.79344100
H	-3.43242100	-0.16793900	-0.00649900
H	-1.42470400	-3.87657900	0.33004400
H	-2.61862100	-2.69962200	0.81689000
H	3.51193000	0.16128700	2.31356300
H	1.87357300	0.05635700	2.93451200
H	2.86115500	1.90922100	0.71324600
H	2.46669000	2.36958000	2.36328200
H	0.15621900	1.33903200	3.01790600
H	0.01712500	3.06611300	2.72136000

H	-1.86310500	2.71233400	1.17936800
H	-2.19499200	2.06723800	2.77600600
H	-2.34994900	-0.05601000	3.21548900
H	-3.12185800	-0.96462400	1.93785500
H	-0.20191900	-1.05834000	2.81755800
H	-1.40943600	-2.32666700	2.97633900
H	0.83253700	-3.20729700	0.09515600
H	0.45600900	-3.72108000	1.74644400
H	1.71631200	-1.94230200	2.73244800
H	2.71130000	-2.74262100	1.53997000
Tl	0.00811000	-0.00024200	-0.32449300

Sum of electronic and zero-point Energies= -1496.434000
Sum of electronic and thermal Energies= -1496.407174
Sum of electronic and thermal Enthalpies= -1496.406229
Sum of electronic and thermal Free Energies= -1496.489490

I3

N	0.93273600	1.43487900	1.49210000
C	-0.12112100	1.57155400	2.52178500
C	-1.51393600	1.87160300	1.94281100
N	-2.00492300	0.94042700	0.88722900
C	-2.83193600	-0.17640100	1.41330000
C	-2.03043800	-1.33850600	1.98980800
N	-1.06809200	-1.93824700	1.03413400
C	-0.05548500	-2.74696200	1.75861600
C	1.30146900	-2.72619500	1.06366100
N	1.81643700	-1.35394600	0.84607400
C	2.19138900	-0.68999400	2.11470400
C	2.18819400	0.83845300	2.02579900
C	1.26235400	2.71179000	0.81935100
C	2.00407900	2.49050500	-0.51609900
O	1.92783300	1.32571200	-1.03606700
O	2.62456000	3.46571900	-0.98738200
C	-2.76830600	1.69053000	-0.14036500
C	-1.91612100	2.36308600	-1.22708800
O	-2.44327100	3.30046500	-1.85887900
O	-0.74471800	1.89552100	-1.44930000
C	-1.73824700	-2.75622400	-0.00286300
C	-2.24803800	-2.01487300	-1.25246100
O	-3.13376400	-2.58602900	-1.91792900
O	-1.71324600	-0.89121500	-1.55678000
C	2.90915800	-1.38865300	-0.14534800
C	2.40623800	-1.61410500	-1.58634700
O	3.23336800	-2.03180900	-2.41799600
O	1.17303700	-1.35443400	-1.84170700
H	0.34735900	3.26110800	0.59409200
H	1.87658400	3.34509100	1.47197600
H	-3.41495000	2.44601700	0.32168500
H	-3.41244700	0.98914100	-0.67455800
H	-2.57548900	-3.31718500	0.43195000
H	-1.02069800	-3.49279800	-0.37796400
H	3.43244800	-0.43098300	-0.14115300
H	3.63475300	-2.17499700	0.10001700

H	0.12665200	2.38386400	3.22014200
H	-0.13841300	0.65239400	3.10995300
H	-1.50804200	2.87671700	1.51641500
H	-2.22285800	1.89874000	2.78082800
H	-3.51320200	0.18739700	2.19528100
H	-3.45685300	-0.54042100	0.59687500
H	-2.74424400	-2.09818400	2.34188600
H	-1.47184400	-1.00683500	2.86607900
H	0.03318900	-2.35956100	2.77473300
H	-0.38548600	-3.78891000	1.85962000
H	2.01571500	-3.31502400	1.65721000
H	1.22326200	-3.20484400	0.08449200
H	3.19210800	-1.00793700	2.43919400
H	1.49971400	-1.01748500	2.89175300
H	2.39848100	1.24337000	3.02460900
H	3.00225600	1.16082200	1.37606100
Tl	0.04596300	0.00276100	-0.32623700

Sum of electronic and zero-point Energies= -1496.437626
Sum of electronic and thermal Energies= -1496.410845
Sum of electronic and thermal Enthalpies= -1496.409901
Sum of electronic and thermal Free Energies= -1496.492460

TS1

N	1.18096400	-1.71556600	1.13221900
C	2.23801900	-1.14912000	2.01479000
C	2.57610300	0.37899400	1.90920300
N	1.78689700	1.25680600	1.00180300
C	1.07742400	2.34491800	1.72944300
C	-0.30571300	1.94594500	2.24623700
N	-1.25106300	1.58961300	1.15835100
C	-2.46512300	0.91504900	1.68850500
C	-2.24673500	-0.55731200	2.03129100
N	-1.80079800	-1.36271000	0.87163400
C	-1.18491400	-2.63995800	1.30173600
C	0.18027600	-2.45122900	1.95691500
C	1.78102200	-2.60012000	0.09739700
C	0.92618700	-2.87503300	-1.15398200
O	0.01597100	-2.02936000	-1.47088100
O	1.20224500	-3.90332500	-1.80302500
C	2.66177700	1.80617600	-0.06500300
C	2.92960900	0.83571200	-1.22509000
O	3.98970400	0.98606400	-1.86567500
O	2.02746200	-0.03403300	-1.49211900
C	-1.61034200	2.77020500	0.33471500
C	-0.76561600	3.02259300	-0.93014300
O	-0.93018800	4.13101200	-1.48090500
O	0.01833100	2.10351300	-1.34571100
C	-2.89435900	-1.59327000	-0.09814000
C	-3.00661900	-0.58727100	-1.25931200
O	-4.08199100	-0.59602200	-1.89373800
O	-2.00221000	0.15826200	-1.52620600
H	2.68918600	-2.11956100	-0.27172200
H	2.06193300	-3.56251100	0.54325500

H	3.62009600	2.14117700	0.34770000
H	2.16542000	2.66565600	-0.51746700
H	-1.59193800	3.68289200	0.94272000
H	-2.63510100	2.64898300	-0.02247700
H	-2.74010500	-2.56553600	-0.57309700
H	-3.86441500	-1.63726900	0.41188400
H	3.16629900	-1.70401000	1.85500100
H	1.94866900	-1.34228600	3.04819300
H	3.62597200	0.46015700	1.61775600
H	2.51022300	0.78580000	2.92167300
H	1.67557500	2.69157100	2.58132200
H	0.97887600	3.19640100	1.05492000
H	-0.70901300	2.78744000	2.82802800
H	-0.22281400	1.10020700	2.93285400
H	-2.82878500	1.43111800	2.58774600
H	-3.24876400	0.99966500	0.93449000
H	-1.50419300	-0.64806700	2.82513400
H	-3.18834900	-0.95681600	2.43525100
H	-1.10285000	-3.27985900	0.42447700
H	-1.83101100	-3.15968600	2.02471300
H	0.06021700	-1.90722200	2.89413800
H	0.57135900	-3.44398200	2.22047600
Tl	-0.00344500	-0.00701000	-0.31654700

Imaginery frequency: -189.30
Sum of electronic and zero-point Energies= -1496.423817
Sum of electronic and thermal Energies= -1496.397927
Sum of electronic and thermal Enthalpies= -1496.396983
Sum of electronic and thermal Free Energies= -1496.477959

TS2a

N	0.92846300	1.52905200	1.44000500
C	-0.19221700	1.96161800	2.31776900
C	-1.50031900	2.25309200	1.56517600
N	-2.01035100	1.13917200	0.73100100
C	-2.80929800	0.14056300	1.48690000
C	-1.98160700	-0.93249100	2.20707200
N	-1.07581800	-1.69015100	1.30867400
C	-0.01555900	-2.39055000	2.07752600
C	1.23891200	-2.58376200	1.24292400
N	1.84311500	-1.30329900	0.78312100
C	2.50172000	-0.56337000	1.89030400
C	2.02243800	0.89463700	2.23276400
C	1.44369700	2.67736200	0.65314800
C	2.28429100	2.26103000	-0.56671500
O	2.04062000	1.11028300	-1.06610500
O	3.11217600	3.08880400	-1.00053300
C	-2.77550200	1.67571200	-0.40998600
C	-1.90915600	2.15640500	-1.57294700
O	-2.44625300	2.91606500	-2.40326100
O	-0.71072600	1.72438700	-1.64077800
C	-1.82044300	-2.62798700	0.43711900
C	-2.32221200	-2.06286000	-0.90602800
O	-3.19730500	-2.73381300	-1.49314100

O	-1.79851000	-0.98492000	-1.34343200
C	2.78192600	-1.59009500	-0.33720600
C	2.09490800	-1.89138100	-1.69307600
O	2.78611800	-2.46932400	-2.55422500
O	0.86975000	-1.52058900	-1.85789500
H	0.59903500	3.24945700	0.26091900
H	2.03024300	3.34650500	1.29287100
H	-3.42813100	2.50052500	-0.09644900
H	-3.40994700	0.88697000	-0.81715500
H	-2.67650100	-3.05441600	0.97542100
H	-1.16784600	-3.46667800	0.17844700
H	3.40508700	-0.71008700	-0.49711400
H	3.43220800	-2.43585400	-0.08155400
H	0.08756000	2.87690800	2.85788200
H	-0.34507700	1.19100600	3.07201900
H	-1.36201100	3.11538000	0.90937500
H	-2.25188100	2.54843100	2.31120800
H	-3.43696200	0.64021800	2.23872900
H	-3.48722300	-0.34315900	0.78207900
H	-2.68436500	-1.61690400	2.70453100
H	-1.37762900	-0.48355900	2.99592100
H	0.21270200	-1.80859100	2.97256000
H	-0.36678400	-3.37100500	2.42612300
H	1.97485100	-3.16033200	1.81931000
H	0.99802100	-3.16972500	0.35242700
H	3.57189700	-0.51516800	1.67919300
H	2.40203400	-1.15546900	2.80292200
H	1.71202500	0.88835500	3.27936400
H	2.89800300	1.54620300	2.18034600
Tl	0.06637500	-0.00663100	-0.28780800

Imaginery frequency: -145.00
Sum of electronic and zero-point Energies= -1496.424975
Sum of electronic and thermal Energies= -1496.399060
Sum of electronic and thermal Enthalpies= -1496.398116
Sum of electronic and thermal Free Energies= -1496.478962

TS2b

N	-1.62517400	-1.52171600	1.06788600
C	-0.85186400	-2.34472800	2.02590000
C	0.52665200	-2.71127100	1.49517500
N	1.36168300	-1.53779300	1.11692200
C	1.90646400	-0.84285600	2.30821900
C	1.88510500	0.73140000	2.35174900
N	1.25205300	1.51620000	1.24743200
C	0.26888100	2.51380200	1.77036300
C	-1.12198800	1.93756400	2.01563300
N	-1.76605900	1.43874700	0.77633900
C	-2.96527500	0.61352600	1.07174100
C	-2.63955200	-0.70200300	1.77347500
C	-2.22028800	-2.35078300	-0.00361300
C	-2.50010100	-1.63679900	-1.34106100
O	-1.83927700	-0.57309800	-1.61543800
O	-3.34175700	-2.16710400	-2.09186400

C	2.41225500	-2.01843800	0.18720600
C	1.86556100	-2.33873100	-1.22198700
O	2.59644000	-3.02107700	-1.96724900
O	0.69731700	-1.90008800	-1.52724500
C	2.27771300	2.19973300	0.41600100
C	2.87071000	1.36694200	-0.72916500
O	3.99910000	1.70158200	-1.14928200
O	2.14404400	0.43936300	-1.21606300
C	-2.12529900	2.53870300	-0.14838600
C	-1.14830300	2.82171900	-1.30353800
O	-1.35246100	3.86885100	-1.95138200
O	-0.22750700	1.96982200	-1.55017600
H	-1.52874000	-3.16201300	-0.24553800
H	-3.15455400	-2.81221800	0.34103300
H	2.88553000	-2.92379800	0.59058300
H	3.18421600	-1.25812200	0.08006800
H	3.08947000	2.58766300	1.04056300
H	1.80789000	3.05255000	-0.08009600
H	-3.07871800	2.29954400	-0.62708400
H	-2.28452500	3.47325800	0.40175800
H	-1.38712400	-3.27219600	2.27487600
H	-0.75789300	-1.78131600	2.95653900
H	0.42289800	-3.33394900	0.60560800
H	1.04771200	-3.31522800	2.25076000
H	1.34052300	-1.18698300	3.17524800
H	2.93910400	-1.16940500	2.46952500
H	2.91786400	1.07434300	2.45798900
H	1.37630500	1.00304900	3.27882900
H	0.63494800	2.95733900	2.70435600
H	0.19876800	3.32757700	1.04764800
H	-1.05974100	1.12030900	2.73685600
H	-1.74112000	2.72226400	2.47438300
H	-3.46602400	0.42066400	0.12320300
H	-3.66748900	1.17164600	1.70812100
H	-2.27045700	-0.49966200	2.78000000
H	-3.57571500	-1.26483000	1.89487800
Tl	-0.00594900	0.00356500	-0.31304700

Imaginery frequency: -180.32
Sum of electronic and zero-point Energies= -1496.422453
Sum of electronic and thermal Energies= -1496.396378
Sum of electronic and thermal Enthalpies= -1496.395434
Sum of electronic and thermal Free Energies= -1496.476898

TS3a

N	0.20542800	1.91166400	1.34030400
C	-0.93151400	1.89691600	2.29539900
C	-2.24544100	1.46520900	1.65078000
N	-2.19744700	0.17432500	0.91659000
C	-2.29413200	-1.03082400	1.77976500
C	-0.95864500	-1.54122500	2.33102200
N	0.08505700	-1.87341200	1.31574700
C	1.40240100	-2.06237800	1.99619800
C	2.59398000	-1.10572300	1.63526500

N	2.40001100	-0.03862600	0.62045200
C	2.65057200	1.30849400	1.19591200
C	1.49698100	1.80178100	2.06621300
C	0.16752600	3.10315900	0.45865200
C	0.84068200	2.95227700	-0.92323000
O	1.08544000	1.77405200	-1.35782300
O	1.08934600	4.01181600	-1.53184400
C	-3.24477700	0.19467000	-0.13467100
C	-2.82998900	0.95054000	-1.41621400
O	-3.75042700	1.30611500	-2.17988100
O	-1.57806100	1.14827200	-1.63055300
C	-0.26374700	-3.09514200	0.53925400
C	-1.22803800	-2.92370100	-0.64779600
O	-1.77882700	-3.96370800	-1.06492400
O	-1.36575800	-1.75863500	-1.15189600
C	3.24015300	-0.25627200	-0.57584200
C	2.64478900	-1.20633500	-1.61768700
O	3.43587000	-1.82143100	-2.35958200
O	1.36932200	-1.25669000	-1.70533900
H	-0.87503400	3.35707600	0.25284300
H	0.61517800	3.96693700	0.96646400
H	-4.17280400	0.63767200	0.24712900
H	-3.46116800	-0.82815000	-0.44298100
H	-0.66647000	-3.86493100	1.20907400
H	0.65646300	-3.49010100	0.10217800
H	3.35395700	0.69883600	-1.09437500
H	4.23996500	-0.61144600	-0.30081300
H	-1.07812100	2.89132000	2.74012300
H	-0.67618200	1.22848600	3.11836900
H	-2.55790100	2.22921100	0.93524200
H	-3.01953700	1.42994000	2.43022700
H	-2.94647800	-0.83511400	2.64198700
H	-2.77394200	-1.82128700	1.20153500
H	-1.17477900	-2.43287300	2.93658800
H	-0.52806000	-0.80373000	3.00770200
H	1.24079800	-1.99412600	3.07420300
H	1.73669600	-3.08398700	1.81032200
H	2.91543500	-0.63565600	2.56840000
H	3.42809300	-1.73456000	1.31305400
H	2.82219300	2.00027200	0.37350600
H	3.56226500	1.30324400	1.80954300
H	1.35446000	1.11868700	2.90756100
H	1.77467800	2.77497600	2.49562900
Tl	-0.01877900	-0.01167100	-0.31603100

Imaginery frequency: -176.14
Sum of electronic and zero-point Energies= -1496.421810
Sum of electronic and thermal Energies= -1496.395671
Sum of electronic and thermal Enthalpies= -1496.394727
Sum of electronic and thermal Free Energies= -1496.476521

TS3b

N	-1.07537000	-1.69056400	1.30826400
C	-0.01505800	-2.39084900	2.07715900

C	1.23959800	-2.58362000	1.24273100
N	1.84342700	-1.30290600	0.78324700
C	2.50153100	-0.56295400	1.89072500
C	2.02225000	0.89517100	2.23275600
N	0.92785700	1.52909700	1.44019900
C	-0.19287600	1.96117600	2.31813100
C	-1.50110900	2.25232700	1.56564800
N	-2.01066200	1.13845800	0.73111700
C	-2.80953300	0.13953000	1.48663500
C	-1.98178500	-0.93361100	2.20663300
C	-1.81940300	-2.62858400	0.43638200
C	-2.32177500	-2.06320600	-0.90642700
O	-1.79833200	-0.98510200	-1.34375500
O	-3.19702100	-2.73407000	-1.49339900
C	2.78253100	-1.58929100	-0.33691600
C	2.09582700	-1.89048700	-1.69293800
O	2.78750900	-2.46759500	-2.55426300
O	0.87039400	-1.52059400	-1.85767500
C	1.44252300	2.67767200	0.65328900
C	2.28346500	2.26167600	-0.56641300
O	3.11119300	3.08969600	-1.00004100
O	2.04025300	1.11086100	-1.06587200
C	-2.77577600	1.67509000	-0.40989400
C	-1.90937600	2.15634400	-1.57262100
O	-2.44645900	2.91629800	-2.40267200
O	-0.71088200	1.72444800	-1.64057300
H	-1.16616200	-3.46661200	0.17719800
H	-2.67505200	-3.05586600	0.97464200
H	3.43292200	-2.43498900	-0.08131600
H	3.40562400	-0.70918000	-0.49652200
H	2.02863700	3.34720100	1.29300600
H	0.59756600	3.24921600	0.26091000
H	-3.40987200	0.88623300	-0.81739800
H	-3.42872800	2.49961200	-0.09627200
H	-0.36612400	-3.37143300	2.42555300
H	0.21299000	-1.80902000	2.97232100
H	0.99904500	-3.16950600	0.35210200
H	1.97560400	-3.16005500	1.81916900
H	2.40132600	-1.15500900	2.80331400
H	3.57183000	-0.51482700	1.68017900
H	2.89769500	1.54683400	2.17966300
H	1.71236100	0.88929900	3.27952000
H	-0.34547700	1.19047700	3.07235800
H	0.08665900	2.87649800	2.85831500
H	-2.25279200	2.54710700	2.31177900
H	-1.36318300	3.11490300	0.91015600
H	-3.48734000	-0.34407600	0.78161900
H	-3.43738300	0.63886300	2.23852400
H	-1.37833600	-0.48486000	2.99601000
H	-2.68454700	-1.61849700	2.70343600
Tl	0.06637700	-0.00667600	-0.28791800

Imaginery frequency: -144.86

Sum of electronic and zero-point Energies= -1496.424987

Sum of electronic and thermal Energies= -1496.399071

Sum of electronic and thermal Enthalpies= -1496.398127

Sum of electronic and thermal Free Energies= -1496.478978

TS4

N	1.15063800	1.44387000	1.40862100
C	0.14215800	1.77519400	2.44208500
C	-1.20114600	2.17820100	1.83621400
N	-1.84779400	1.13403500	0.99008500
C	-2.71266100	0.20939200	1.77371900
C	-2.33547600	-1.31180800	1.85977900
N	-1.24316900	-1.84001900	0.99985500
C	-0.29466800	-2.65726900	1.80477900
C	1.09097300	-2.77588500	1.17786700
N	1.70747100	-1.45933700	0.89368200
C	2.14540400	-0.77800400	2.13319800
C	2.33278700	0.73123200	1.96272500
C	1.61605200	2.62177300	0.64317100
C	2.24554900	2.23432800	-0.70976400
O	1.97518300	1.07309400	-1.16808800
O	2.96979900	3.08860700	-1.26218600
C	-2.64336100	1.79933000	-0.07951100
C	-1.81189000	2.41055300	-1.22365800
O	-2.36128400	3.29048900	-1.91601500
O	-0.62197600	1.96102600	-1.41219900
C	-1.77469300	-2.64129100	-0.12722600
C	-2.39638900	-1.81467400	-1.26379400
O	-3.35386800	-2.30872500	-1.89015400
O	-1.84396400	-0.68938800	-1.53107100
C	2.77836000	-1.62781300	-0.10178900
C	2.22632900	-1.87713300	-1.51385200
O	3.00065600	-2.38597500	-2.34665900
O	1.01202100	-1.54048900	-1.74567900
H	0.77507200	3.27885400	0.42023400
H	2.34368700	3.20115500	1.22570400
H	-3.28579800	2.58014900	0.34715600
H	-3.28424900	1.04989500	-0.54636100
H	-2.50899900	-3.37272100	0.23071900
H	-0.94760600	-3.19523600	-0.58288400
H	3.37960600	-0.71935900	-0.15346800
H	3.44131900	-2.45938100	0.17063700
H	0.49575100	2.60025000	3.07724900
H	0.01895500	0.90646500	3.09386500
H	-1.05866400	3.06346400	1.21432300
H	-1.87496500	2.47790100	2.64843800
H	-2.77074900	0.57688000	2.80192300
H	-3.72505400	0.27812800	1.37232700
H	-3.24857800	-1.88362200	1.66212800
H	-2.06880200	-1.52034600	2.89650300
H	-0.21273500	-2.19895500	2.79105500
H	-0.69488000	-3.66865400	1.96251200
H	1.72964500	-3.36023800	1.85639500
H	1.04129900	-3.32950200	0.23836200
H	3.09207200	-1.20287400	2.49659300
H	1.39936700	-0.97003100	2.90620100
H	2.60533900	1.16032900	2.93644400

H	3.17267800	0.91707800	1.29175300
Tl	0.01431800	0.00092200	-0.29519400

Imaginery frequency: -182.71
Sum of electronic and zero-point Energies= -1496.426590
Sum of electronic and thermal Energies= -1496.400578
Sum of electronic and thermal Enthalpies= -1496.399634
Sum of electronic and thermal Free Energies= -1496.480394

TS5

Tl	0.00876000	0.05135700	-0.39162200
N	1.94843900	0.73699600	1.27635000
C	2.30359100	-0.41517700	2.13198000
C	2.30884100	-1.71093200	1.32803600
N	0.96742600	-2.07377500	0.81759800
C	0.11832900	-2.55831900	1.93143500
C	-1.35351400	-2.66546500	1.55563600
N	-1.88323000	-1.41176100	0.97319800
C	-2.28304700	-0.47863500	2.05213500
C	-2.30283500	0.99181200	1.65074700
N	-0.97429300	1.58086300	1.33013800
C	-0.05423400	1.65795200	2.49213200
C	1.39445200	1.86818200	2.05238000
C	3.12596700	1.18120000	0.49760700
C	2.82301400	1.62782200	-0.93992000
O	1.79069400	1.13538400	-1.50124200
O	3.65662400	2.38496500	-1.48464400
C	1.10064000	-3.10645800	-0.22778400
C	1.37970500	-2.55965900	-1.63270500
O	0.90159200	-1.40566000	-1.92692700
O	1.99442000	-3.29404800	-2.42805500
C	-2.99488100	-1.68562600	0.04356900
C	-3.03421100	-0.82426300	-1.22263300
O	-1.93738300	-0.29602400	-1.61698200
O	-4.11809800	-0.76356900	-1.83901600
C	-1.19010700	2.93231200	0.74899500
C	-1.27267600	2.98678900	-0.78690400
O	-0.70547200	2.05441100	-1.43511400
O	-1.83164300	3.99255000	-1.27934500
H	1.59857400	-0.47671400	2.96142500
H	3.29437100	-0.26920400	2.58283200
H	2.97690000	-1.61004600	0.46860500
H	2.71140900	-2.52188900	1.95191100
H	0.23054600	-1.87452100	2.77355800
H	0.46846600	-3.54080800	2.28027300
H	-1.49569300	-3.46579000	0.82951000
H	-1.91865800	-2.96156600	2.45137000
H	-1.61237800	-0.62880400	2.90008500
H	-3.29076900	-0.72939700	2.41523300
H	-2.92833300	1.12463800	0.76278700
H	-2.77089500	1.56618700	2.46210000
H	-0.14487000	0.74568000	3.08087500
H	-0.34659700	2.48371400	3.15385400
H	1.46237900	2.75637900	1.41956100

H	2.01093000	2.06587300	2.94067400
H	3.66770400	1.97144200	1.02960300
H	3.82025400	0.34228500	0.39250200
H	1.87143300	-3.84029000	0.03684400
H	0.15833100	-3.65299200	-0.31637200
H	-2.88524400	-2.70327000	-0.34378900
H	-3.96750000	-1.64476100	0.55012600
H	-2.09265400	3.38239100	1.17590900
H	-0.35573200	3.58201400	1.02329500

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Imaginery frequency: -75.80
Sum of electronic and zero-point Energies=          -1496.418779
Sum of electronic and thermal Energies=             -1496.392483
Sum of electronic and thermal Enthalpies=           -1496.391539
Sum of electronic and thermal Free Energies=        -1496.474357
```

Crystal structure analysis

Several efforts to crystallize $[Tl^{III}(dota)]^-$ with various metal counter ions and solvents were unsuccessful. Finally our earlier technique[1] became fruitful and its guanidine salt gave nice X-ray quality crystals: A colorless prism crystal (0.45 mm x 0.25 mm x 0.25 mm) of $\{C(NH_2)_3\}[Tl(dota)]\cdot H_2O$ was mounted on top of a glass capillary using epoxy glue. Diffraction intensity data collection was carried out at 293(2) K on a Bruker-Nonius MACH3 diffractometer equipped with a point detector using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The structure was solved by SIR-92 program[2] and refined by full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters using the SHELXL-97 package,[3] publication material was prepared with the WINGX- suite.[4] Hydrogen atoms were located geometrically and refined in the rigid mode except water hydrogens which could be found at the difference electron density map. The distance of the hydrogen and oxygen atoms had to be restrained in the final stage of the refinement. The orientation of the water molecules, hence the description of the hydrogen bond web is uncertain and some B and C level errors remained in the checkcif. The remaining electron density peaks are close to the Thallium. Crystallographic and X-ray experimental details are summarized in Tables S1-S3. Tables were prepared using the PublCIF software. Packing diagram is shown at Figure S6.

References

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3 G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

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Table S2: Crystal data

$C_{16}H_{24}N_4O_8Tl \cdot CH_6N_3 \cdot H_2O$	$Z = 2$
$M_r = 682.86$	$F(000) = 672$
Triclinic, $P\bar{1}$	$D_x = 1.996$ Mg m^{-3}
$a = 7.498$ (10) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 12.406$ (5) Å	Cell parameters from 25 reflections
$c = 12.800$ (4) Å	$\theta = 6.4$–$15.3°$
$\alpha = 91.01$ (1)°	$\mu = 7.17$ mm^{-1}
$\beta = 90.86$ (4)°	$T = 293$ K
$\gamma = 107.31$ (6)°	Prism, colourless
$V = 1136.3$ (17) Å^3	0.45 × 0.25 × 0.25 mm

Table S3: Data collection

Enraf-Nonius MACH3 diffractometer	$R_{int} = 0.046$
ω–θ–scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.9°$
Absorption correction: ψ scan North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta. Cryst. A24, 351 Number of ψ scan sets used was 3 Theta correction was applied. Averaged transmission function was used. Fourier smoothing - Window value 5	$h = -3 \rightarrow 9$
$T_{min} = 0.556$, $T_{max} = 0.987$	$k = -15 \rightarrow 14$
4909 measured reflections	$l = -15 \rightarrow 15$
4464 independent reflections	3 standard reflections every 182 reflections
4117 reflections with $I > 2\sigma(I)$	intensity decay: 10%

Table S4: Refinement details

Refinement on F^2	19 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.156$	$w = 1/[\sigma^2(F_o^2) + (0.0992P)^2 + 10.8511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
4464 reflections	$\Delta\rangle_{max} = 3.58$ e Å^{-3}
331 parameters	$\Delta\rangle_{min} = -4.05$ e Å^{-3}