Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Probing the Coordination Environment of Ti^{3+} Ions Coordinated to Nitrogen Containing Lewis Bases

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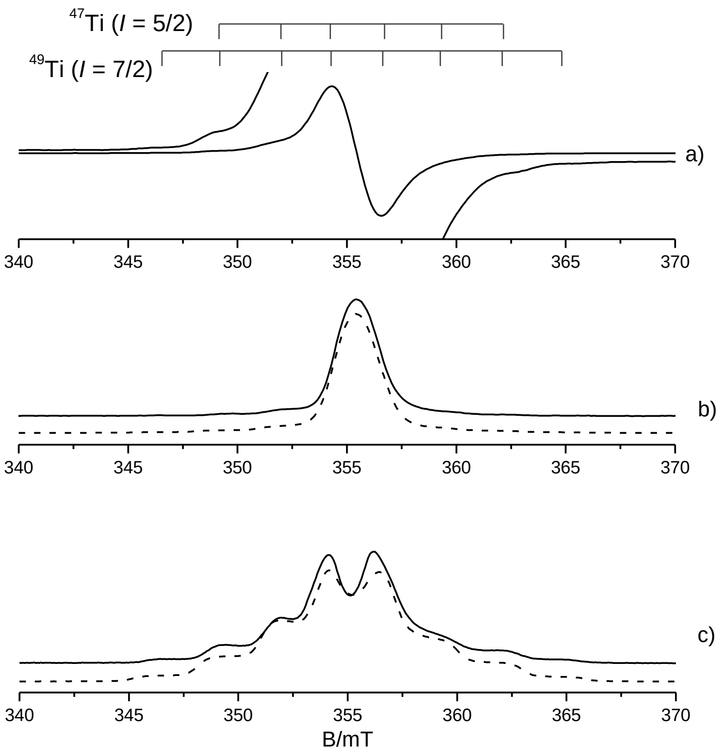

Figure 1S Experimental (solid line) and simulated (dotted line) spectra of a frozen diluted solution of $TiCl_3$ in 1-methyl imidazole: a) CW-EPR; b) ESE-detected EPR recorded using $t_{\pi/2}$=16 ns and an inter-pulse delay τ= 200 ns; c) ESE-detected EPR recorded using the same pulse length and τ = 1200 ns. All spectra are recorded at 10K. The simulation of spectrum b) is performed considering all Ti isotopes in their natural abundance, while in c) only the magnetically active ^{47}Ti and ^{49}Ti isotopes are considered.

The reason why at larger pulse delays the central line disappears can be explained considering that the phase memory time (T_m) for a given S=1/2 species depends on the number of coupled nuclei with spin I, which is the reason why Tm of a deuterated system is longer than for the corresponding protonated system. A detailed discussion on this subject can be found in: A. Schweiger, G. Jeschke in Principles of Pulse Paramagnetic Resonance, Oxford University Press (Oxford, UK) 2001, ch. 8 p. 214.

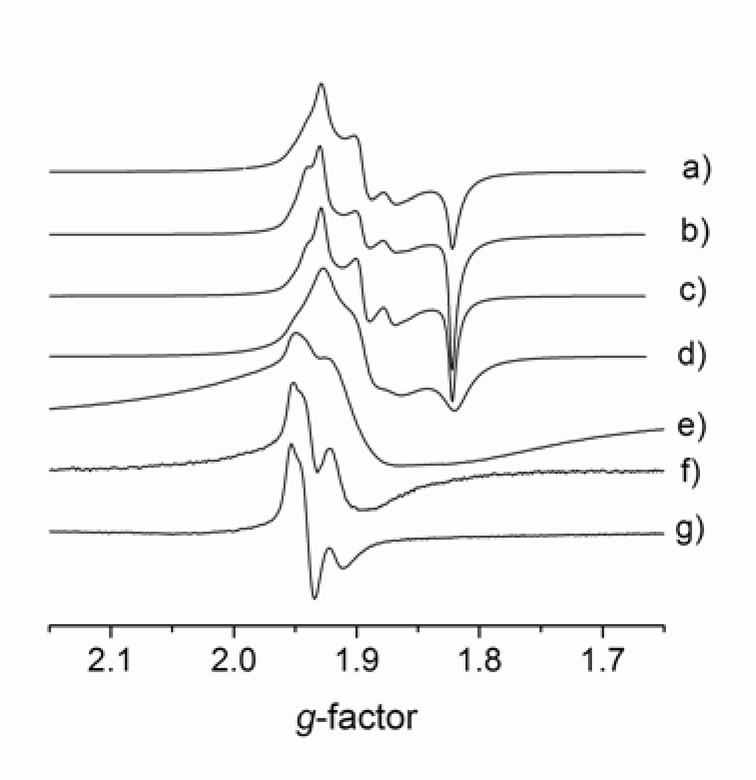

Figure 2S. Variable temperature X-band CW EPR spectra of the solid-state $Ti(Py)_3Cl_3$ complex. The spectra are recorded respectively at temperature of (a) 10 K, (b) 20 K, (c) 50 K, (d) 120K, (e) 180 K, (f) 250 K, (g) 300 K. The spectral changes are due to a gradual population of the triplet (S=1) state at higher temperatures. Similarly, W-band CW EPR experiments proved to be difficult at temperatures above 30K due to the presence of high concentrations of the triplet state in the undiluted powder.

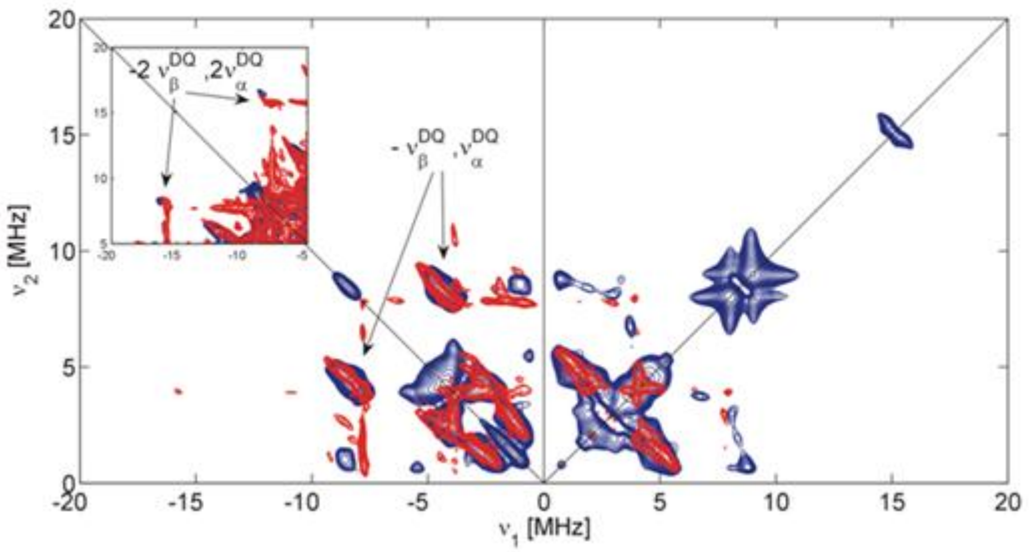

Figure 3S. Experimental (blue line) and simulated (red line) *X*-band HYSCORE spectra of a frozen solution of $TiCl_3$ dissolved in 1-methyl imidazole. The spectrum is taken at τ = 96 + 120ns and observer position B_0 = 355.0mT. The parameters extracted from the computer simulation are listed in Table 2 of the main text.

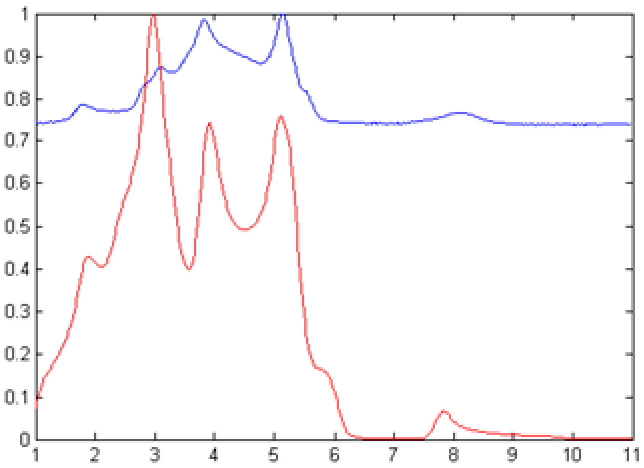

Figure 4S. Davies ENDOR spectrum of a $TiCl_3$/imidazole diluted frozen solution recorded at the maximum echo intensity. The experimental settings are $t_{\pi/2}$=100 ns, t_{π} =200 ns, $t_{\pi RF}$=10300 ns. The length of the RF pulse was optimized for the 3.8 MHz and 5.18 MHz transitions by nutation experiments. Blue experimental, red simulated.

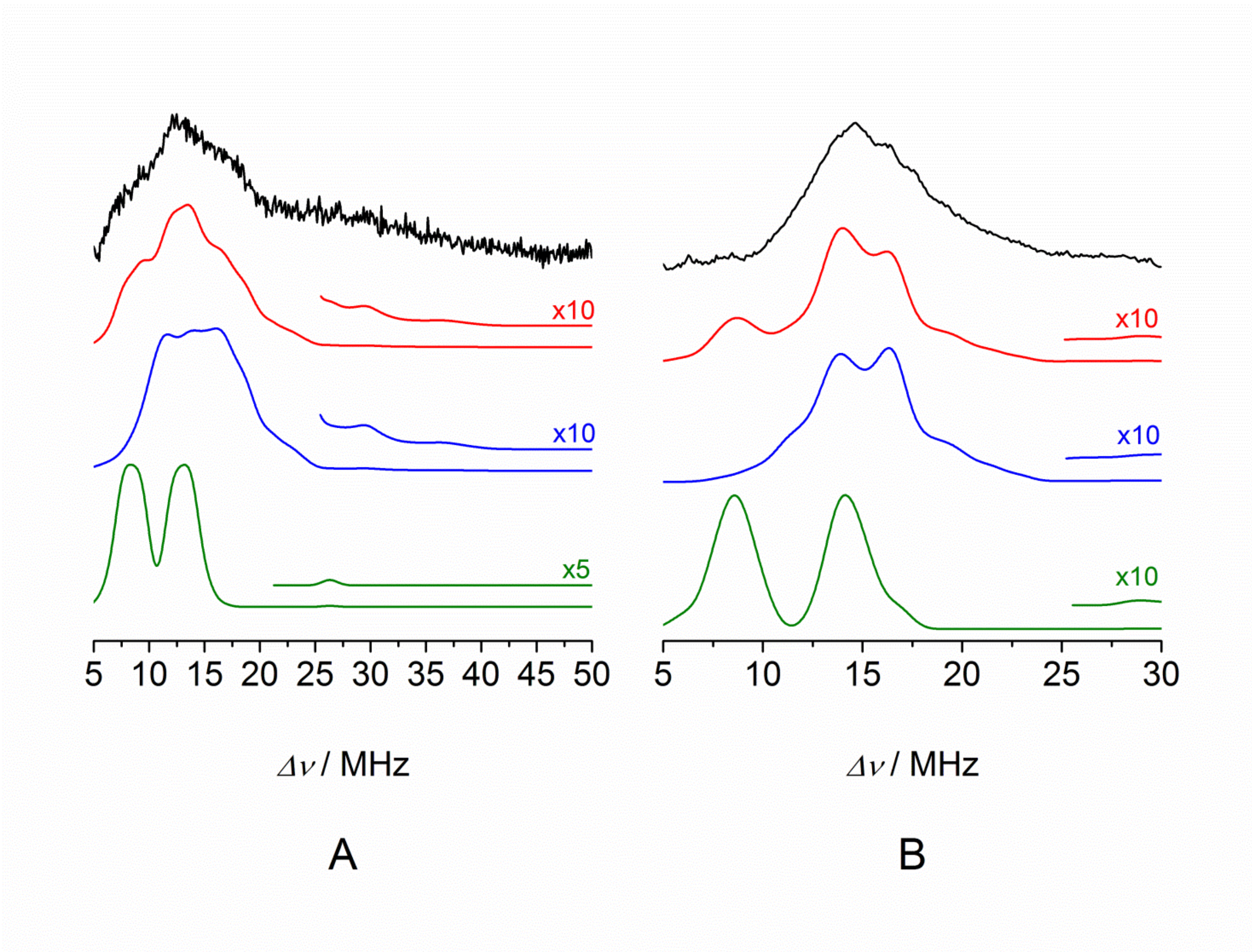

Figure 5S. Experimental (black line) and computer simulated (red line) W-band EDNMR spectrum of the solid state $TiCl_3(Py)_3$ complex (panel A) and of the $TiCl_3$ 1-methyl imidazole frozen solution (panel B). The spectra were recorded at 5K, at field position (A) B_0=3462mT and (B) B_0=3700mT. The deconvolution of the $^{35,37}Cl$ (blue line) and the ^{14}N (green line) contribution is shown. The spin Hamiltonian parameters extracted from the simulation are listed in Table 1S.

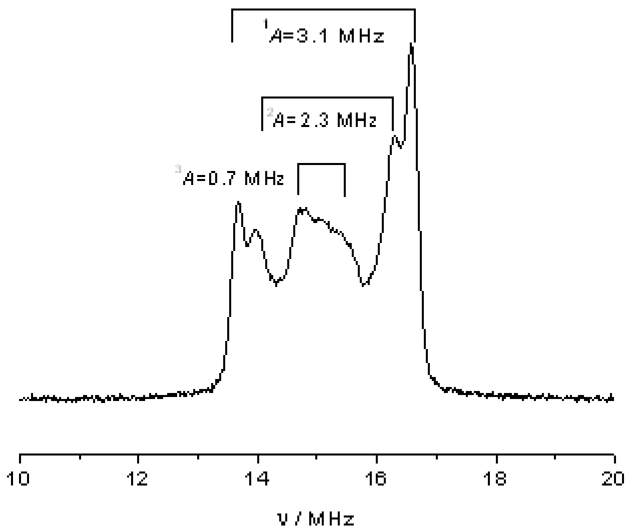

Figure 6S. [1]H Davies ENDOR spectrum of a $TiCl_3$/imidazole diluted frozen solution recorded at the maximum echo intensity. The experimental settings are $t_{\pi/2}$=100 ns, t_{π} =200 ns, $t_{\pi RF}$=7000 ns. The length of the RF pulse was optimized at 15.1 MHz by means of nutation experiments.

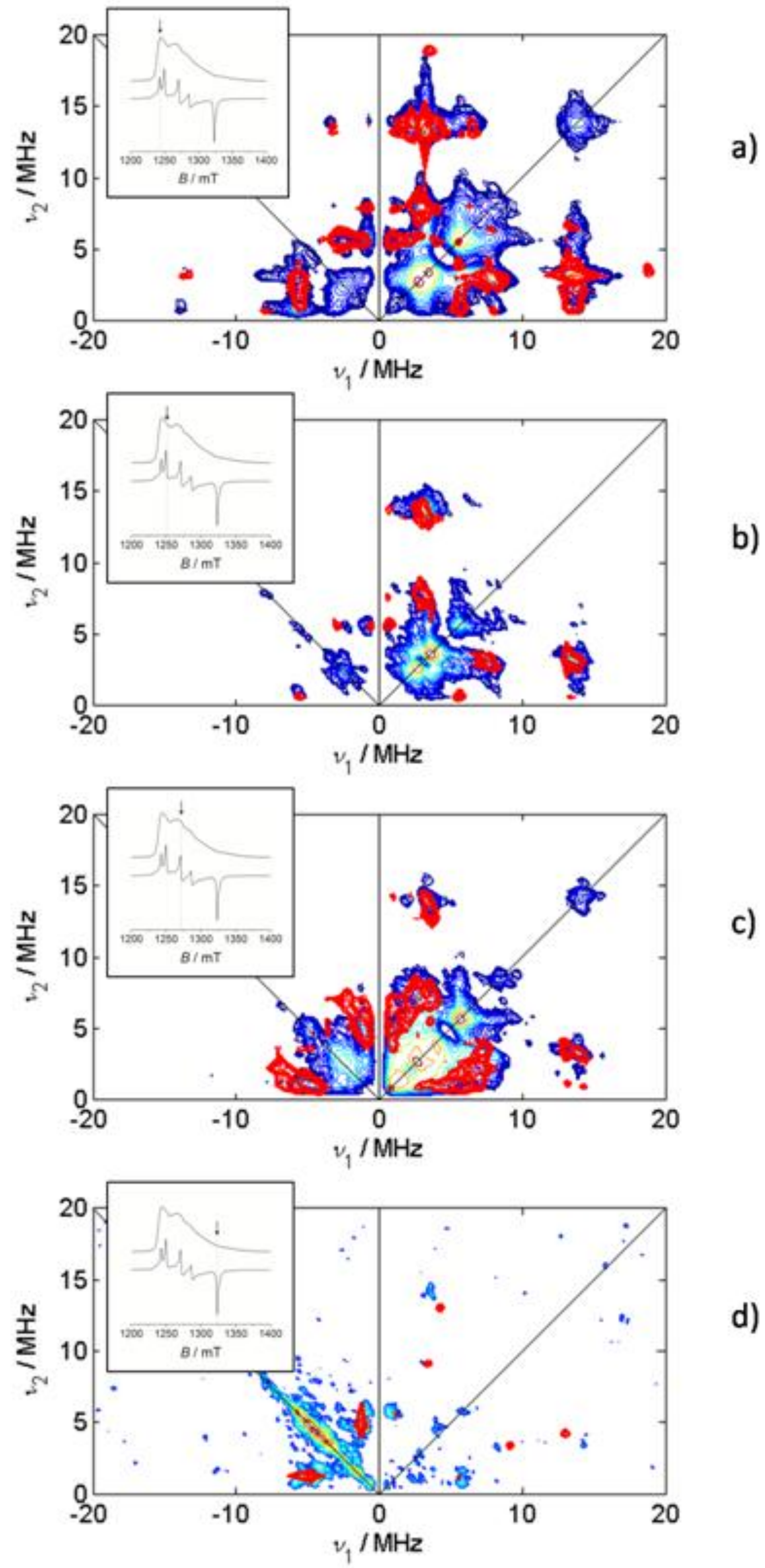

Figure 7S. Experimental (blue lines) and computer simulated (red lines) Q-band HYSCORE spectra of the solid-state $Ti(Py)_3Cl_3$ complex recorded at field positions corresponding to (a) 1243.3 mT (g = 1.944), (b) 1252.0 mT (g = 1.930), (c) 1274.0 mT (g = 1.897) and (d) 1327.5 mT (g = 1.822) as shown in the insets. The spectra are recorded at T = 10K and τ = 260ns. The simulation was carried out considering a three spin system (S= 1/2, I=1, I=1).

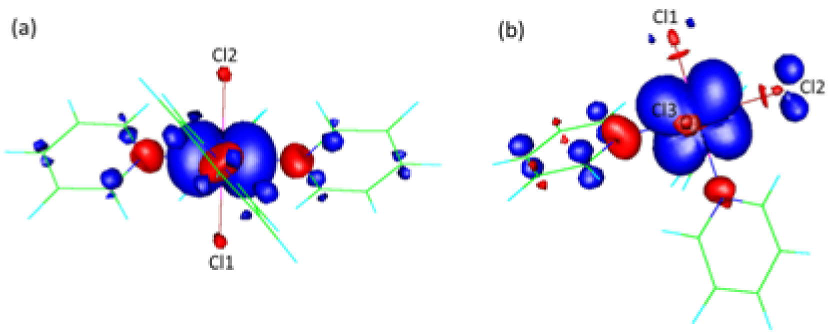

Figure 8S. Spin density plots (blue positive, red negative) for (a) $[Ti(Py)_4Cl_2]^+$ and (b) $Ti(Py)_3Cl_3$. The computed hyperfine coupling tensors for chlorine nuclei in (a) are: ***A***(Cl1)=[-1.78 -1.78 -2.63] MHz and ***A***(Cl2)=[-1.79 -1.79 -2.63] MHz; (b) ***A***(Cl1)=[-6.46 3.67 -3.59] MHz; ***A***(Cl2)=[9.21 -4.39 -8.48] MHz; ***A***(Cl3)=[-2.85 0.87 -5.21] MHz. Spin densities are displayed for an isosurface value of 0.0015.

Table 1S. Spin-Hamiltonian parameters employed for the simulation of the EDNMR spectra of $TiCl_3(Py)_3$ solid complex and $TiCl_3$ 1-methyl imidazole frozen solution. Hyperfine and quadrupole values are given in MHz.

		$\|A_1\|$	$\|A_2\|$	$\|A_3\|$	$\|e^2qQ/h\|$	η
$Ti(Py)_3Cl_3$ solid	^{14}N	4.5 ± 1	4.5 ± 1	5.5 ± 1	3.0 ± 0.5	0.1 ± 0.1
	$^{35,37}Cl$	9 ± 2	8 ± 2	5 ± 2	15 ± 3	0.3 ± 0.2
$TiCl_3$ in 1-methyl imidazole	^{14}N	5 ± 2	5 ± 2	8 ± 2	2.7 ± 1	0.6 ± 0.3
	$^{35,37}Cl$	2 ± 2	2 ± 2	3 ± 2	13 ± 3	0.7 ± 0.3

Table 2S. DFT-computed ^1H hyperfine tensors for representative 1-methyl imidazole complexes complexes. Values are given in MHz.

	A_x	A_y	A_z
$[Ti(1\text{-}MeIm)_6]^{3+}$	2.44	3.09	-2.88
$[Ti(1\text{-}MeIm)_4Cl_2]^+$	-3.45	-3.13	1.69

Table 3S. DFT-computed *g* tensors for different model complexes.

Model	g_x	g_y	g_z
$[Ti(1\text{-}MeIm)_6]^{3+}$	1.9106	1.9212	1.9940
$[Ti(1\text{-}MeIm)_4Cl_2]^+$	1.8922	1.8948	1.9713
$Ti(1\text{-}MeIm)_3Cl_3$	1.8876	1.9055	1.9918
$[Ti(1\text{-}MeIm)_5(OH)]^{2+}$	1.9648	1.9731	1.9760
$[Ti(Py)_6]^{3+}$	1.8374	1.8791	1.9929
$[Ti(Py)_5Cl]^{2+}$	1.9379	1.9459	1.9725
$[Ti(Py)_4Cl_2]^+$	1.9502	1.9502	1.9717
$Ti(Py)_3Cl_3$	1.9035	1.9126	1.9932
$Ti(Py)_3(OH)Cl_2$	1.9534	1.9708	1.9759

Table 4S. DFT-computed ^{14}N and ^{1}H hyperfine tensors for model complexes containing coordinated OH groups.

Model		A_x (MHz)	A_y (MHz)	A_z (MHz)	e^2qQ/h (MHz)	η
$[Ti(1\text{-}MeIm)_3(OH)]^{2+}$	N1	-5.77	-6.80	-6.20	2.08	0.845
	N2	-6.70	-6.08	-5.65	2.07	0.805
	N3	-8.01	-7.89	-8.70	2.04	0.835
	OH	2.01	10.68	0.60	-	-
$[Ti(1\text{-}MeIm)_5(OH)]^{2+}$	N1	-7.10	-5.44	-5.95	-2.32	0.717
	N2	-5.95	-5.59	-6.42	-2.28	0.780
	N3	-5.89	-6.17	-6.63	-2.34	0.721
	N4	-2.54	-2.68	-1.97	-2.36	0.739
	N5	-7.08	-5.36	-5.89	-2.33	0.711
	OH	-5.36	-3.64	3.91	-	-
$Ti(Py)_3(OH)Cl_2$	N1	-5.50	-7.58	-5.17	-3.12	-0.016
	N2	-5.35	-4.99	-7.12	-3.15	0.016
	N3	-6.89	-4.84	-5.21	-3.16	0.021
	OH	-3.50	-5.97	7.06	-	-

DFT-optimized geometries of the Ti(III) complexes studied in this work (coordinates given in Å)

$[Ti(1\text{-}MeIm)_6]^{3+}$

N	0.641733	-3.335330	3.493835
C	0.528680	-2.663669	2.324382
N	0.459970	-1.334425	2.538017
C	-2.650863	0.493135	-0.040831
C	1.986668	-1.666816	-0.984217
C	1.812593	-2.633436	-1.953653
N	-1.811635	-0.147318	0.800364
C	0.094720	3.785265	-1.526919
N	0.224331	2.789681	-2.482008
C	0.287166	1.601720	-1.835569
N	0.208399	1.776157	-0.500967
C	0.088345	3.149879	-0.302468
C	0.288493	2.989695	-3.930212
Ti	0.313440	0.225684	1.029412
C	0.711795	2.462626	3.275946
N	-0.192440	1.671975	2.568774
C	-1.410539	1.974944	3.058448
N	-1.319453	2.911316	4.031402
C	0.018806	3.234768	4.184510
C	-2.435148	3.484179	4.785165
N	0.739170	-1.262261	-0.518442
C	-0.167499	-1.985701	-1.206328
C	-2.595251	-1.064780	1.498250
C	-3.898951	-0.965552	1.062024
N	-3.911504	0.024084	0.090042
C	-5.083991	0.475033	-0.661146
N	0.447029	-2.820597	-2.079319
C	-0.223696	-3.753810	-2.989249
H	-2.378121	1.290741	-0.739541
H	2.920879	-1.248696	-0.598108
H	2.533998	-3.195767	-2.555320
H	0.017754	4.843486	-1.796844
H	0.399287	0.644689	-2.355773
H	0.003003	3.590664	0.695675
H	0.371803	2.006442	-4.424774

H	-0.629348	3.499467	-4.277998
H	1.171239	3.605641	-4.184947
H	1.789825	2.426305	3.093217
H	-2.361809	1.535941	2.741078
H	0.359267	3.975114	4.915614
H	-3.373896	3.007262	4.454110
H	-2.491449	4.573629	4.602149
H	-2.290242	3.298862	5.865844
H	-1.255317	-1.931251	-1.094977
H	-2.178668	-1.727197	2.262752
H	-4.805666	-1.505427	1.353464
H	-4.781845	1.288367	-1.343271
H	-5.496902	-0.365794	-1.249229
H	-5.853805	0.848406	0.039562
H	-0.808565	-4.492789	-2.410610
H	-0.895850	-3.200312	-3.670860
H	0.543355	-4.280213	-3.582270
N	2.433763	0.611804	1.231174
C	3.141728	1.558091	0.577865
C	4.597337	0.497163	1.864708
N	4.443117	1.517258	0.936900
C	3.349134	-0.058747	2.041196
C	5.504746	2.393440	0.439909
H	2.742702	2.278421	-0.143682
H	5.567835	0.261207	2.312983
H	3.055972	-0.885487	2.694665
H	5.074973	3.097579	-0.293322
H	6.290340	1.786992	-0.048173
H	5.945250	2.960356	1.281251
C	0.533506	-1.166077	3.918563
C	0.644024	-2.402480	4.519299
C	0.746631	-4.786221	3.650878
H	0.507800	-3.162973	1.350071
H	0.502783	-0.178649	4.389609
H	0.722321	-2.695487	5.571239
H	0.720225	-5.257928	2.653303
H	-0.100321	-5.159539	4.256542
H	1.698842	-5.040737	4.152836

$[Ti(1\text{-}MeIm)_4Cl_2]^+$

H	-2.668419	1.741361	1.281010
H	0.370960	3.535936	-0.170727
H	1.038893	2.726929	-5.091470
H	0.280733	4.412923	-2.834037
C	0.275086	3.404796	-2.406680
C	0.322773	2.958450	-1.099700
H	1.935611	-4.155485	4.946416
H	-0.080817	-2.137850	5.578017
C	-0.077898	-0.845394	3.719265
H	-5.922477	0.244085	1.569978
H	-5.155602	1.849257	1.285438
C	-5.330076	0.847149	0.855505
N	-4.041374	0.207670	0.603479
C	-3.843061	-1.056779	0.074191
C	-2.816545	0.746216	0.846932
H	6.145075	1.418419	2.909861
H	4.902961	2.689888	3.202929

C	5.439980	2.119974	2.424253
H	2.608275	1.964681	2.567943
C	3.119301	1.383991	1.791863
N	4.468393	1.382830	1.620555
C	4.751386	0.557021	0.545273
C	3.534675	0.079749	0.096264
H	5.775704	0.383355	0.199404
H	3.320951	-0.608192	-0.728274
H	6.007746	2.824074	1.786294
N	-1.839264	-0.105170	0.502954
Cl	-0.079282	2.081341	2.098111
Ti	0.341479	0.240808	0.685272
N	0.288334	1.570937	-1.086694
N	0.398000	-1.106347	2.441975
Cl	0.762476	-1.601352	-0.724763
N	2.517867	0.602688	0.882930
C	-2.474502	-1.239547	0.017215
H	-1.904160	-2.100284	-0.346952
H	-4.678101	-1.705000	-0.211345
H	-5.896052	0.951852	-0.089957
C	0.143640	-1.947153	4.523395
N	0.762755	-2.891526	3.721204
C	0.898081	-2.349920	2.481197
C	1.191029	-4.226592	4.130518
H	0.322027	-4.816095	4.480468
H	1.649994	-4.737287	3.265598
H	1.346012	-2.881826	1.634391
C	0.221021	1.191766	-2.371244
N	0.211264	2.270718	-3.199114
C	0.145879	2.237427	-4.657848
H	-0.763798	2.759383	-5.011785
H	0.112190	1.185314	-4.991739
H	0.189551	0.155767	-2.726763
H	-0.534672	0.117046	3.971994

$[Ti(Py)_6]^{3+}$

H	2.243172	-5.178247	-0.393674
H	3.486109	-7.262460	-0.904264
H	3.012699	-9.142988	0.859442
H	1.066528	-10.584837	0.309782
H	1.290536	-12.307775	-1.545077
H	5.387405	-10.986902	-2.076658
H	3.517279	-12.483988	-2.757181
H	8.938553	-8.955131	1.473667
H	5.745432	-11.839810	0.810588
H	6.890937	-14.030944	0.514242
H	8.336474	-8.205682	-2.045185
H	4.154890	-8.337968	-2.440475
H	4.017919	-8.499348	2.452416
N	4.918052	-7.021567	0.620194
C	5.328324	-6.234453	1.656905
C	4.671163	-5.055985	2.019213
C	3.546721	-4.646538	1.283938
C	3.118221	-5.447159	0.214204
C	3.820458	-6.620764	-0.078491
Ti	6.075546	-8.840099	0.074542
N	5.913811	-9.392513	2.247549

C	4.805691	-9.060484	2.969747
C	4.645727	-9.388768	4.318148
C	5.673700	-10.078898	4.978678
C	6.824043	-10.419666	4.250555
C	6.901622	-10.069343	2.900509
C	7.451768	-8.103186	-2.685181
C	7.610039	-7.765156	-4.031311
C	6.469357	-7.607223	-4.833568
C	5.209273	-7.804642	-4.248433
C	5.135252	-8.156191	-2.898332
N	6.234449	-8.304348	-2.104941
N	7.854603	-7.536604	0.357981
C	8.942407	-7.932288	1.074556
C	10.040482	-7.099788	1.313559
C	10.037280	-5.800718	0.782971
C	8.924343	-5.384682	0.033811
C	7.858978	-6.269639	-0.149256
N	4.303016	-10.002266	-0.564033
C	4.417210	-10.925331	-1.563585
C	3.365547	-11.761799	-1.942946
C	2.136062	-11.659966	-1.270040
C	2.007021	-10.711209	-0.244227
C	3.103068	-9.902233	0.071575
N	7.264142	-10.704027	-0.103847
C	8.487623	-10.742487	-0.699753
C	9.193401	-11.931213	-0.909979
C	8.629280	-13.141463	-0.478332
C	7.373552	-13.112691	0.151713
C	6.726812	-11.886324	0.317598
H	3.721982	-9.095737	4.836149
H	5.579932	-10.346648	6.041551
H	7.661110	-10.960127	4.713914
H	7.786973	-10.354279	2.318463
H	4.281295	-7.696459	-4.826920
H	6.560853	-7.336367	-5.895848
H	8.622667	-7.624842	-4.434283
H	9.161444	-14.092995	-0.625606
H	10.175538	-11.895517	-1.401473
H	8.924153	-9.785782	-1.015232
H	6.976291	-5.961055	-0.726691
H	8.870651	-4.379103	-0.406198
H	10.887923	-5.123311	0.949274
H	10.884707	-7.479266	1.905856
H	3.012667	-3.720138	1.542143
H	5.047708	-4.469363	2.868789
H	6.212134	-6.569220	2.217793

$[Ti(Py)_4Cl_2]^+$

Cl	-1.167055	0.642387	1.223851
H	2.278389	-2.589300	0.738215
H	1.233070	-4.552652	4.471513
H	-1.518872	-1.929281	2.366751
H	-1.041283	-3.429907	4.313758
C	-0.271383	-3.271739	3.545209
C	-0.546811	-2.436068	2.456690
N	0.355408	-2.194409	1.469370

H	-1.192985	-1.098550	-3.199722
H	-1.781054	0.339256	-5.163802
H	-1.517757	2.859029	-4.965673
H	-0.673180	3.805762	-2.763823
H	-0.147360	2.229810	-0.890161
H	-5.502791	-3.784722	-0.997955
H	-5.402573	-1.246077	-0.934999
H	-3.184238	-0.129273	-0.614339
H	5.208399	2.097473	0.499530
H	2.275883	0.103992	-2.012328
C	4.251663	1.570281	0.366385
C	3.410851	1.319970	1.462844
C	3.844211	1.133074	-0.904073
C	2.620002	0.466716	-1.032678
C	-4.545296	-3.259540	-0.862831
N	1.802168	0.221493	0.024842
Ti	-0.145188	-0.848161	-0.246927
N	-2.094072	-1.915422	-0.517662
C	-3.257141	-1.226140	-0.654778
C	-2.149323	-3.272764	-0.551678
C	-4.494564	-1.856847	-0.828226
C	-3.346853	-3.977264	-0.721071
C	2.202023	0.646498	1.252224
H	4.463667	1.303163	-1.796254
H	3.680910	1.640354	2.478921
H	1.516797	0.443108	2.088340
H	-3.329556	-5.076220	-0.740097
H	-1.192337	-3.804754	-0.447418
Cl	0.874821	-2.339809	-1.717359
C	-1.097981	-0.004307	-3.140022
C	-1.419978	0.804679	-4.235868
C	-1.273070	2.196506	-4.121838
C	-0.806914	2.723937	-2.907023
C	-0.505956	1.848227	-1.857410
N	-0.645937	0.500478	-1.962020
C	1.571273	-2.795430	1.555135
C	1.922765	-3.644184	2.611140
C	0.986445	-3.890176	3.628195
H	2.921762	-4.102193	2.627123