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

Electronic Supplementary Information (ESI)

Time-dependent DFT study of K-edge spectra for vanadium and titanium complexes: Effects of chloride ligands on pre-edge features

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Peak broadening using pseudo Voigt function

To compare the calculated K-edge spectra with the experiments, we estimated peak broadening based on the pseudo-Voigt broadening scheme. The pseudo-Voigt function is an approximation of the Voigt profile. It is often used for calculations of experimental spectral line shapes. The normalized pseudo-Voigt function is of a form

$$V_p(x) = (1-\eta)\cdot G(x) + \eta \cdot L(x) \tag{1}$$

where G(x) and L(x) are the normalized Gaussian and Lorentzian functions, the η is a parameter which mixes the two functions. The normalized Gaussian and Lorentzian functions are given by

$$G(x) = \frac{1}{c\sqrt{2\pi}} e^{-\frac{x^2}{2c^2}} \quad \text{where} \quad c = \frac{f}{2\sqrt{2ln2}} \tag{2}$$

$$L(x) = \frac{f}{2\pi x^2 + 0.25 \times f^2} \tag{3}$$

Here, we employed the same full width at half maximum (FWHM), denoted as f, for both Gaussian and Lorentzian profiles in the pseudo-Voigt function and for all the peaks in the pre-edge region.

Table S1. The root-mean-square error (φ) between the experimental and calculated geometrical parameters under different function (LC-BLYP, CAM-B3LYP and ωB97XD) for vanadium and titanium complexes.

	LC-BLYP		CAM-B3LYP		ωB97XD	
	φ(BL)[a]	φ(BA)[b]	φ(BL)	φ(BA)	φ(BL)	φ(BA)
Complex **3**	0.06	1.5	0.04	1.7	0.04	1.3
Complex **4**	0.04	1.3	0.02	0.5	0.03	0.8
Complex **5**	0.04	0.9	0.03	1.1	0.04	0.9
Complex **6**	0.05	1.1	0.04	1.4	0.04	1.2
Complex **7**	0.05	1.2	0.04	1.3	0.04	1.1
Complex **9**	0.05	1.4	0.05	1.5	0.05	1.1
Complex **10**	0.04	1.9	0.01	1.8	0.01	1.4
Complex **11**	0.03	1.9	0.01	1.8	0.01	1.4

[a] Root-mean-square error of bond length between calculated and experimental data

[b]Root-mean-square error of bond angle between calculated and experimental data.

$$\varphi = \sqrt{\frac{\sum_{i}^{n}(X_{ci} - X_{ei})^2}{n}}$$

, where X_{ci} is the calculated value for each bond length or bond angle and X_{ei} is the experimental value for each bond length or bond angle. The subscripts c and e represent calculated and experimental, respectively, and i is the serial number of each bond length or bond angle.

Table S2. The root-mean-square error (φ) between experimental and calculated geometrical parameters, as well as some selected bond length and bond angle of the complexes **5** and **6**.

Bond length [Å]				
Complex **5**	Experimental	LC-BLYP	CAM-B3LYP	ωB97XD
V-N1	1.652	1.579	1.604	1.599
V-N2	2.224	2.246	2.273	2.280
V-N3	1.858	1.830	1.852	1.849
V-Cl1	2.268	2.235	2.254	2.254
V-Cl2	2.271	2.239	2.257	2.258
φ(BL)		0.042	0.032	0.035
Bond angle [°]				
Complex **5**	Experimental	LC-BLYP	CAM-B3LYP	ωB97XD
V-N1-C1	170.94	176.22	171.21	172.76
N1-V-N2	174.90	178.68	176.69	175.07
N2-V-N3	78.20	77.14	77.52	77.12
N1-V-N3	97.41	101.55	99.29	98.03
Cl1-V-Cl2	119.95	116.23	118.75	119.34
Cl1-V-N3	116.92	118.13	117.20	117.12
Cl2-V-N3	118.18	118.19	117.56	117.35
φ(BA)		0.94	1.14	0.93
Bond length [Å]				
Complex **6**	Experimental	LC-BLYP	CAM-B3LYP	ωB97XD
V-N1	1.654	1.596	1.619	1.614
V-N2	2.221	2.262	2.282	2.289
V-N3	1.886	1.872	1.891	1.887
V-C25	2.092	2.041	2.064	2.063
V-C26	2.091	2.039	2.063	2.060
φ(BL)		0.046	0.036	0.040
Bond angle [°]				
Complex **6**	Experimental	LC-BLYP	CAM-B3LYP	ωB97XD
V-N1-C1	176.36	176.22	175.54	177.64
N1-V-N2	177.73	178.68	179.28	177.43
N2-V-N3	78.08	77.14	77.17	76.62
N1-V-N3	99.65	101.55	102.12	100.82
C25-V-C26	116.81	116.23	116.04	116.68

C25-V-N3	118.11	118.13	118.26	117.96
C26-V-N3	120.02	118.19	118.21	117.91
φ(BA)		1.14	1.40	1.18

Table S3. The pre-edge peak energies and intensity of the vanadium complexes **1-9**.

Complex	Experimental [a]		Calculated		Expt. Intensity		Cal. Intensity	
	E_{P1}/eV	E_{P2}/eV	E_{P1}/eV	E_{P2}/eV	P_1	P_2	P_1	P_2
1	5465.0	5466.8	5465.0	5467.1	0.20	0.38	3.04	7.23
2	5465.6	5467.1	5465.0	5467.2	0.22	0.40	2.89	7.31
3	5466.4		5467.0		0.50		7.67	
4	5465.1	5466.6	5465.1	5467.3	0.18	0.52	4.31	7.73
5	5465.2	5467.3	5464.9	5467.6	0.21	0.28	2.89	4.83
6	5465.0	5467.1	5464.4	5467.5	0.15	0.51	4.29	5.81
7	5465.5	5467.5	5465.5	5467.8	0.21	0.38	3.41	4.97
8	5466.4		5465.5		0.34		6.34	
9	5467.1		5467.2		0.27		4.85	

[a] Experimental energies as reported in Ref.18. E_{P1} is the energy of the first peak and E_{P2} is the energy of the second peak.

Table S4. The pre-edge peak energies and intensity of the titanium complexes **10-12**.

Complex	Experimental [a]		Calculated		Expt. Intensity		Cal. Intensity	
	E_{P1}/eV	E_{P2}/eV	E_{P1}/eV	E_{P2}/eV	P_1	P_2	P_1	P_2
10	4966.1		4966.1		0.16		1.83	
11	4966.1	4967.5	4966.5	4967.9	0.15	0.13	1.63	1.30
12	4966.1	4967.8	4966.2	4967.9	0.17	0.33	2.31	4.74

[a] Experimental energies as reported in Ref. 19. E_{P1} is the energy of the first peak and E_{P2} is the energy of the second peak.

Table S5. The absorption intensity and p-hybridization ratio for each excited state of complexes **1a**–**1d** and **10a**–**10d**.

Complexes \ Excited States	1	2	3	4	5
	p-hybridization ratio (R_h)				
1a	0.0159	0.0125	0.0180	0.0062	0.0520
1d	0.0124	0.0204	0.0201	0.0316	0.0753
1c	0.0182	0.0192	0.0576	0.0525	0.0321
1d	0.0292	0.0175	0.1080	0.0281	0.1465
10a	0.0096	0.0102	0.0087	0.0040	0.0041
10b	0.0091	0.0164	0.0179	0.0057	0.0199
10c	0.0106	0.0333	0.0240	0.0163	0.2001
10d	0.0203	0.0192	0.0321	0.2215	0.0782
	Absorption Intensity ($\times 10^{-4}$)				
1a	0.8963	1.0093	1.1336	0.0186	4.1822
1d	0.6227	1.9935	2.2842	1.2450	3.4434
1c	0.9011	1.9889	2.5713	4.3757	2.0087
1d	1.8221	1.7578	7.1063	1.6773	1.4297
10a	0.4930	0.5100	0.3172	0.1654	0.1436
10b	0.3801	0.3773	0.9157	0.1451	1.5823
10c	0.3190	0.9289	0.8185	0.6840	2.4621
10d	0.7523	0.7912	0.7067	2.3074	1.6867

Table S6. The vanadium p hybridization ratio in the molecular orbital which related to the electron transition in each excited states for complexes **5**, **6** and **7**.

Pre-edge	Vanadium p hybridization ratio	
	P_1	P_2
Complex **5**	0.0444	0.0518
Complex **6**	0.0786	0.2633
Complex **7**	0.0410	0.2153

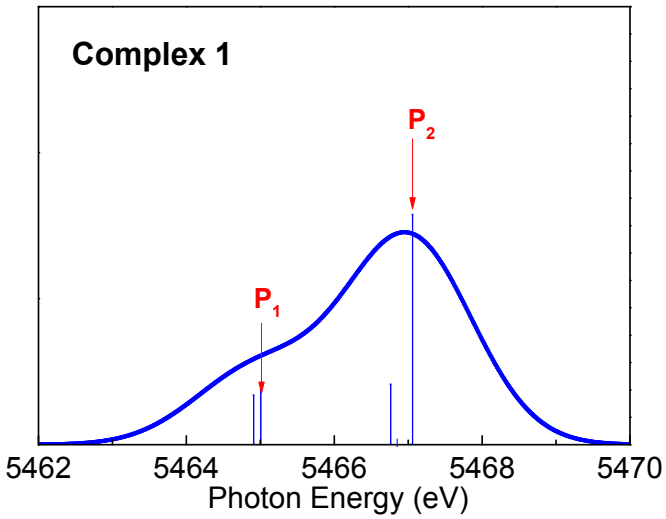

Fig. S1. Definitions of two peaks in the pre-edge region of XANES spectra of complex **1** as an example. Excited state energies which exhibited relatively larger oscillator strengths were identified as P_1 and P_2 to compare with experimental peak values.

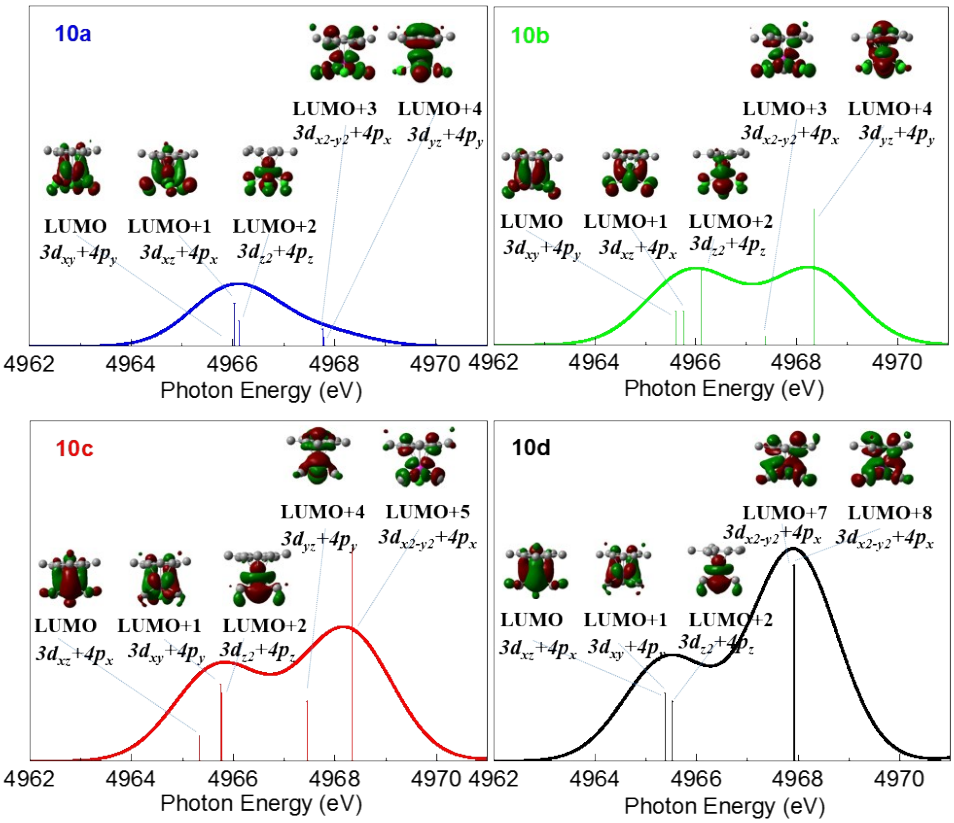

Fig. S2. The pre-edge region of titanium complexes **10a**–**10d**, as well as some related molecular orbitals.

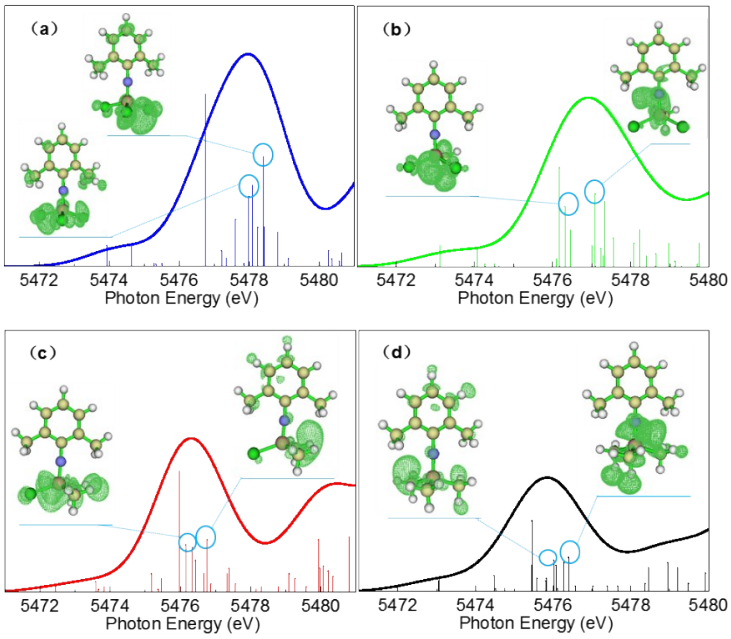

Fig. S3. The electron density difference map ($\Delta\rho_{ex}$) of the second and third strongest excited states in the shoulder peak region for vanadium **1a**–**1d**.

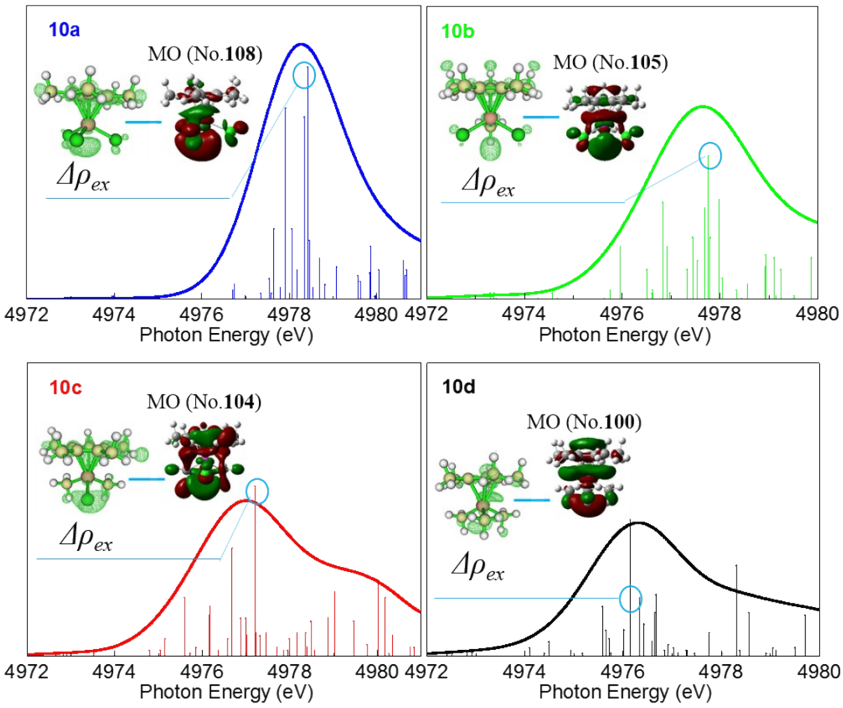

Fig. S4. The electron density difference map ($\Delta\rho_{ex}$) of the strong excited states in the shoulder peak region for titanium complexes **10a**–**10d**, and the related molecular orbitals.

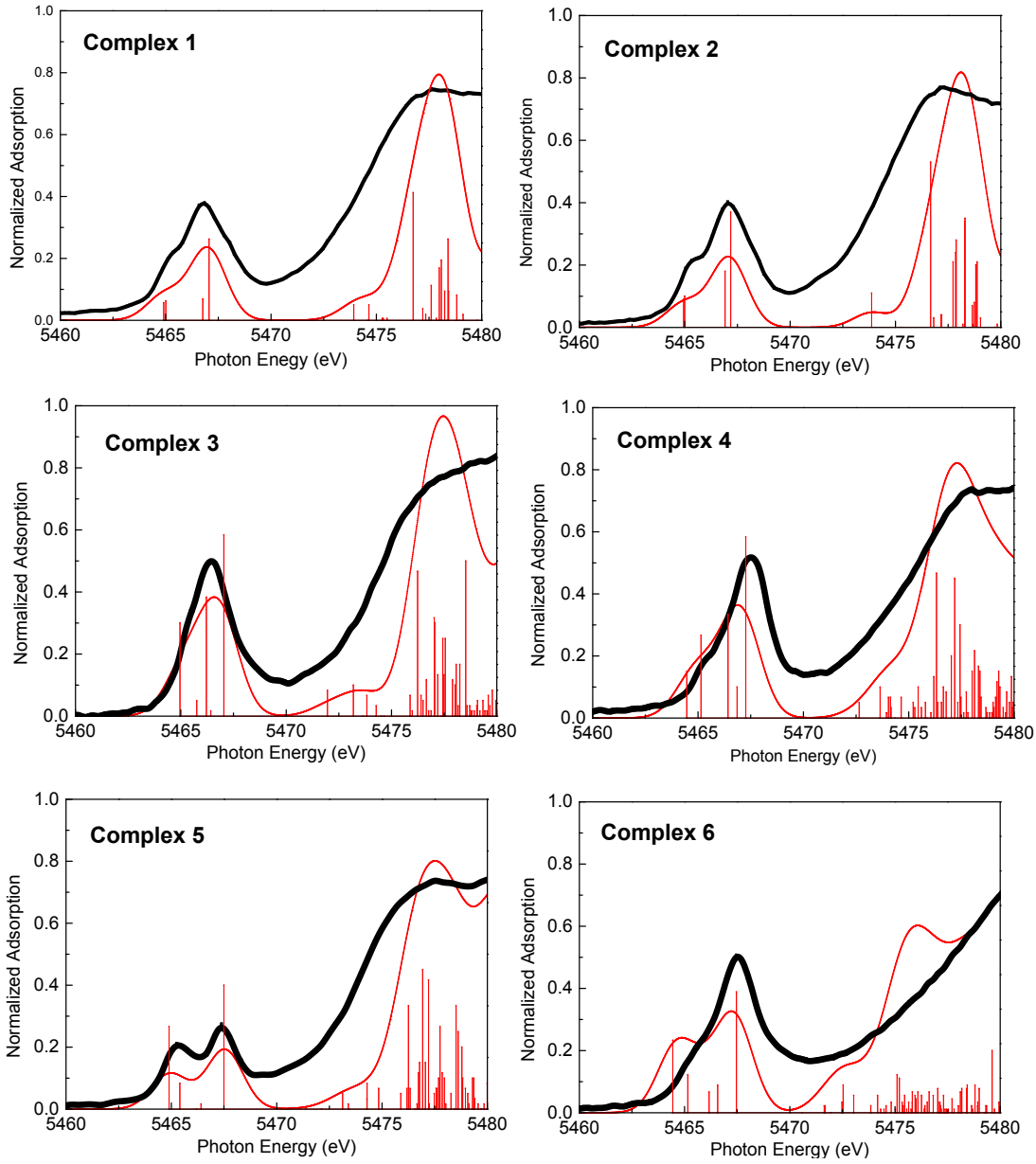

Fig. S5(A). The experimental (black line) and calculated (red line) vanadium XANES spectrum for complexes **1-6**.

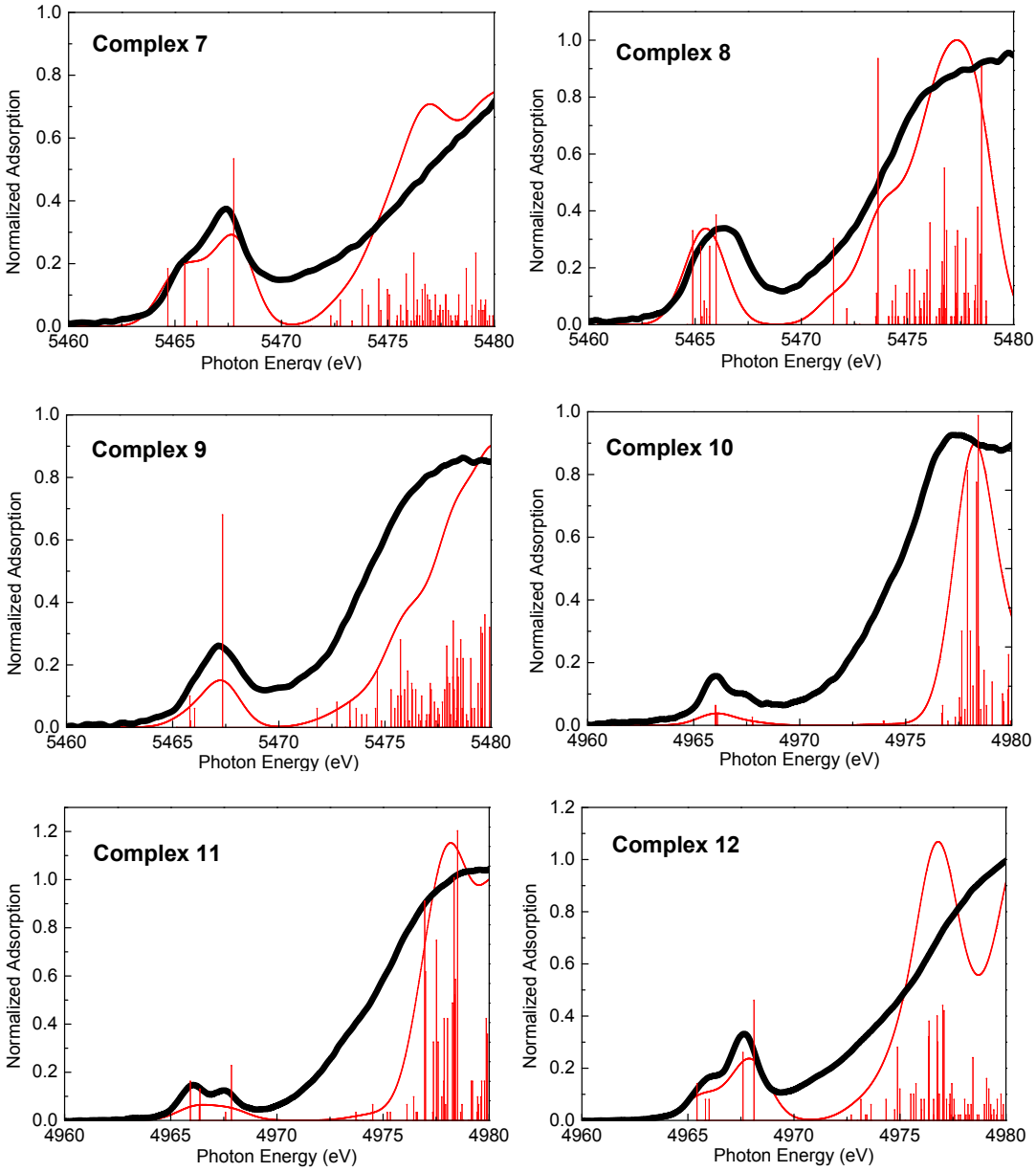

Fig. S5(B). The experimental (black line) and calculated (red line) vanadium XANES spectrum for complexes **7**-**12**.

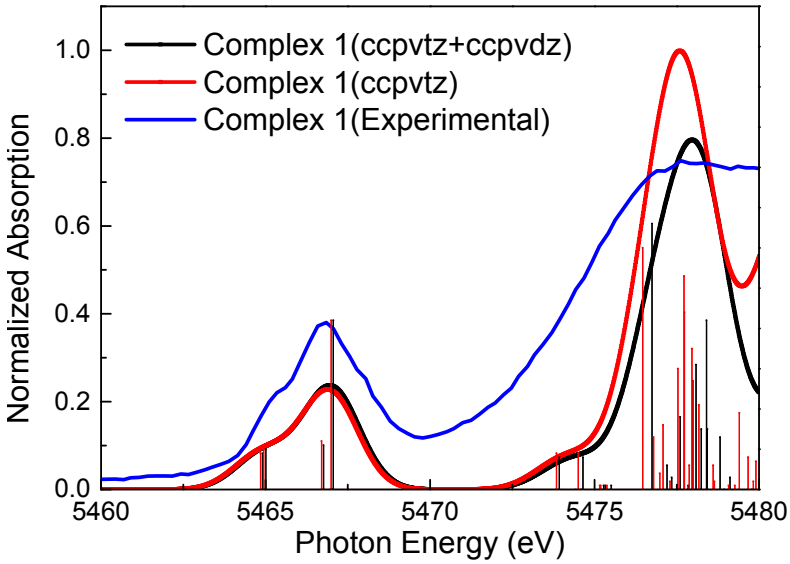

Fig. S6. Basis set dependency in ligand atoms for the K-edge spectra of complex **1**. Calculated spectra with larger basis sets (cc-pVTZ) agreed very well with that with smaller basis sets (cc-pVDZ), particularly for the pre-edge region. The same basis set (cc-pVTZ) was employed for V atom.

Optimized geometries of complexes **1**-**12**:

Complex 1

V	1.48519	0.01638	-0.00002
Cl	2.22634	2.0486	-0.00379
Cl	2.03651	-1.07017	-1.79023
N	-0.11001	0.07771	0.0008
C	-1.48988	0.03953	0.00049
C	-2.20113	1.25823	-0.00015
C	-3.59344	1.18842	-0.00113
C	-4.24716	-0.04162	-0.00095
C	-3.52138	-1.23148	-0.00002
C	-2.128	-1.22025	0.00057
C	-1.46857	2.56921	0.00238
C	-1.32304	-2.48944	0.00107
H	-4.1711	2.1147	-0.00195
H	-5.33801	-0.07445	-0.00162
H	-4.0445	-2.18948	0.00005
H	-2.17282	3.41086	-0.01702
H	-0.83454	2.6663	0.89708
H	-0.79975	2.65246	-0.86775
H	-0.67121	-2.54436	-0.88397
H	-0.67017	-2.54313	0.88542
H	-1.98067	-3.3683	0.00204
Cl	2.03886	-1.06554	1.79219

Complex 2

V	-2.0816	0.0035	0.01065
N	-0.48948	0.01957	0.10238
C	0.94692	0.00824	0.07056
C	1.40578	-0.21407	-1.38592
C	1.47342	1.36316	0.58769
C	1.47009	-1.14916	0.94418
C	2.94244	-0.20407	-1.43544
C	3.45834	1.14715	-0.92218
C	3.00907	1.34772	0.53398
C	3.52318	0.20488	1.42424
C	3.00631	-1.14103	0.89403
C	3.48957	-1.33485	-0.55143
H	1.0135	-1.17984	-1.7423
H	0.98118	0.57029	-2.03174
H	1.06247	2.17141	-0.03713

H	1.11923	1.52547	1.61774
H	1.11161	-1.02774	1.97808
H	1.07005	-2.09873	0.55563
H	3.2545	-0.36416	-2.47868
H	3.05222	1.9597	-1.54752
H	4.55624	1.199	-1.00002
H	3.39709	2.30643	0.91089
H	3.16274	0.35934	2.45518
H	4.62418	0.2073	1.46595
H	3.39243	-1.95778	1.52279
H	3.17518	-2.31653	-0.94167
H	4.59186	-1.31692	-0.56921
Cl	-2.76809	1.85976	0.89626
Cl	-2.53591	-0.12107	-2.10347
Cl	-2.73199	-1.76354	1.08498

Complex 3

V	-0.16943	1.51747	0.39479
Cl	-0.0615	2.28131	2.46496
Cl	-0.16484	3.11936	-1.12255
N	-1.45224	0.56088	0.22179
N	1.11933	0.35761	0.08645
C	-2.44796	-0.37593	0.04277
C	-2.66921	-1.33361	1.05577
C	-3.65922	-2.29099	0.83946
C	-4.40598	-2.2944	-0.33743
C	-4.17588	-1.33514	-1.32138
C	-3.19541	-0.35745	-1.15394
C	-1.84954	-1.30684	2.31513
C	-2.92937	0.69148	-2.19637
C	2.02607	-0.47434	-0.20604
C	2.721	-1.21691	0.96402
C	4.25216	-1.24123	0.82193
C	2.16234	-2.65378	1.03758
C	2.39071	-0.5141	2.29009
C	2.36256	-0.65973	-1.71007
C	3.54231	0.27533	-2.04697
C	2.70973	-2.1076	-2.09354
C	1.15243	-0.2396	-2.56196
H	-3.84906	-3.0434	1.6078
H	-5.17845	-3.05088	-0.48722
H	-4.76802	-1.34153	-2.23898

H	-2.17914	-2.08454	3.0167
H	-0.78298	-1.46914	2.09387
H	-1.91787	-0.32853	2.81361
H	-3.0354	1.70281	-1.77585
H	-1.89822	0.62271	-2.57633
H	-3.62104	0.5883	-3.04285
H	4.60106	-1.76622	-0.07588
H	4.67989	-1.76152	1.69264
H	4.66549	-0.22149	0.8099
H	2.5054	-3.12268	1.97275
H	2.49532	-3.28735	0.20693
H	1.06134	-2.64739	1.04869
H	1.31547	-0.53047	2.51079
H	2.91628	-1.02685	3.11
H	2.70681	0.53893	2.28168
H	3.73093	0.24153	-3.13139
H	4.46998	-0.01483	-1.53643
H	3.30441	1.3152	-1.77681
H	3.58937	-2.50312	-1.57111
H	2.93146	-2.13879	-3.1713
H	1.86213	-2.78505	-1.91266
H	0.92562	0.82863	-2.45588
H	0.25267	-0.81017	-2.28377
H	1.37126	-0.43768	-3.6221

Complex 4

V	-3.81459	1.14844	0.7962
Cl	-4.35226	1.01859	2.88293
Cl	-4.98235	2.49924	-0.42177
N	-3.93518	-0.27858	0.09427
C	-3.96067	-1.44259	-0.64159
C	-4.45058	-2.61274	-0.02637
C	-4.35238	-3.80123	-0.74592
C	-3.76812	-3.82216	-2.01162
C	-3.29438	-2.65025	-2.59972
C	-3.38818	-1.42953	-1.93375
C	-4.98291	-2.56144	1.37554
C	-2.83451	-0.16531	-2.52896
H	-4.71655	-4.72697	-0.29678
H	-3.67051	-4.76759	-2.54736
H	-2.82388	-2.68583	-3.58318
H	-5.37161	-3.54002	1.68511

H	-4.1826	-2.26884	2.07472
H	-5.78763	-1.81772	1.47534
H	-3.57064	0.65079	-2.49381
H	-1.94144	0.17181	-1.97823
H	-2.5305	-0.32699	-3.56963
C	0.37603	0.7949	0.05398
C	0.10819	2.07574	-0.3541
H	0.75581	2.80395	-0.8273
C	-1.78698	1.32101	0.54864
C	-1.79091	3.66948	-0.21037
C	-1.90784	4.19264	-1.49486
C	-2.26112	4.36029	0.90407
C	-2.52467	5.42912	-1.6634
H	-1.5366	3.62471	-2.34918
C	-2.88706	5.5913	0.72162
H	-2.12727	3.93676	1.90141
C	-3.01973	6.12392	-0.5591
H	-2.62921	5.84788	-2.66503
H	-3.26499	6.13692	1.58677
H	-3.50839	7.08906	-0.69912
C	-1.04896	-0.88764	1.29374
C	-1.10572	-0.88091	2.6871
C	-1.21538	-2.06779	0.58062
C	-1.2959	-2.08025	3.36686
H	-0.97371	0.05341	3.22892
C	-1.38376	-3.26695	1.26696
H	-1.22113	-2.04715	-0.50561
C	-1.42108	-3.27553	2.65898
H	-1.33215	-2.07877	4.45686
H	-1.48435	-4.19458	0.7029
H	-1.54917	-4.21733	3.19467
N	-0.83087	0.35719	0.59847
N	-1.18477	2.3891	-0.02183
B	1.77207	-0.05283	-0.13881
C	1.32687	-1.35131	-1.06635
C	1.35319	-2.69539	-0.70023
C	0.69832	-1.10811	-2.29024
C	0.78843	-3.71438	-1.46672
C	0.11872	-2.08856	-3.08114
C	0.1538	-3.41155	-2.65965
C	2.48275	-0.43575	1.2919
C	3.63219	-1.22707	1.29494

C	2.13659	0.0816	2.5348
C	4.34417	-1.55262	2.44025
C	2.81154	-0.22326	3.71286
C	3.92141	-1.05239	3.66683
C	2.88244	0.925	-0.88861
C	3.2723	2.12114	-0.2793
C	3.59551	0.62003	-2.049
C	4.24669	2.97567	-0.77973
C	4.58163	1.44503	-2.58508
C	4.90891	2.63401	-1.95049
F	3.37914	-0.51774	-2.72298
F	5.21809	1.09669	-3.70409
F	5.84684	3.43341	-2.45378
F	4.55021	4.1106	-0.14674
F	-0.49378	-1.77445	-4.23071
F	0.59712	0.15259	-2.75424
F	-0.43448	-4.36395	-3.38449
F	0.78698	-4.97238	-1.01807
F	2.68991	2.51313	0.87041
F	1.82958	-3.09113	0.48629
F	4.09899	-1.71464	0.13558
F	5.42381	-2.33298	2.37857
F	4.58375	-1.35561	4.78193
F	2.40547	0.28776	4.87873
F	1.11091	0.95006	2.66733

Complex 5

V	1.01089	-0.78011	-0.04645
N	-0.58456	-0.68304	-0.05695
N	1.37943	1.03141	0.00968
C	-2.00986	-0.77211	-0.02649
C	-2.40089	-2.25956	-0.16285
C	-2.5426	-0.22208	1.31202
C	-2.61933	0.03117	-1.19252
C	-3.93058	-2.38754	-0.12879
C	-4.46054	-1.8385	1.20481
C	-4.07243	-0.35846	1.34147
C	-4.67731	0.44351	0.17828
C	-4.14894	-0.10687	-1.15579
C	-4.53759	-1.58703	-1.29154
C	4.14111	-1.76106	-0.00085
C	5.51478	-1.58737	0.04302

C	6.02068	-0.28702	0.0977
C	5.13713	0.78311	0.10459
C	3.76717	0.51729	0.05718
C	2.72265	1.59105	0.05929
C	0.37796	2.05373	0.01029
C	-0.13859	2.50828	1.23585
C	-1.12152	3.50165	1.21379
C	-1.57615	4.0326	0.00993
C	-1.05343	3.56876	-1.19374
C	-0.07395	2.57209	-1.21538
C	0.31859	1.90076	2.53529
C	0.43736	2.0199	-2.5189
H	-1.99074	-2.65345	-1.1061
H	-1.93789	-2.82627	0.66024
H	-2.0806	-0.78053	2.14161
H	-2.24978	0.8342	1.41039
H	-2.32475	1.08722	-1.09811
H	-2.21312	-0.34941	-2.14354
H	-4.20166	-3.45016	-0.22812
H	-4.04307	-2.41763	2.04509
H	-5.55707	-1.94748	1.24956
H	-4.44766	0.03746	2.2984
H	-4.41434	1.50998	0.2779
H	-5.77765	0.37466	0.20542
H	-4.57904	0.46828	-1.99068
H	-4.1765	-1.98649	-2.25394
H	-5.63545	-1.69141	-1.28908
H	3.68356	-2.75057	-0.044
H	6.17557	-2.45368	0.0354
H	7.09732	-0.11335	0.1354
H	5.49348	1.81317	0.14689
H	2.84351	2.21638	0.96341
H	2.8898	2.26602	-0.80077
H	-1.53815	3.85878	2.15847
H	-2.34338	4.80872	0.00995
H	-1.41856	3.97638	-2.13927
H	1.40411	2.00873	2.68307
H	-0.18528	2.37578	3.38787
H	0.10803	0.82054	2.5626
H	1.53333	2.08322	-2.59731
H	0.18223	0.95355	-2.62013
H	0.00525	2.56264	-3.37027

N	3.28982	-0.72636	0.00697
Cl	1.23946	-1.94535	1.87443
Cl	1.31424	-1.83022	-2.01794

Complex 6

V	1.09047	-0.96679	0.01509
N	-0.5229	-0.92308	0.02518
N	1.49623	0.8757	0.03531
C	-1.95155	-0.9202	0.00609
C	-2.47217	-2.36688	-0.14246
C	-2.50053	-0.3214	1.31894
C	-2.45712	-0.07689	-1.18399
C	-4.01103	-2.36903	-0.171
C	-4.54905	-1.76715	1.13971
C	-4.03843	-0.3232	1.29086
C	-4.52401	0.52371	0.10029
C	-3.99393	-0.08002	-1.21275
C	-4.50309	-1.52451	-1.36045
C	4.22244	-1.97118	-0.04678
C	5.59987	-1.81471	-0.05096
C	6.11975	-0.51795	-0.00917
C	5.24308	0.55764	0.0337
C	3.86711	0.3089	0.03379
C	2.8445	1.40661	0.07854
C	0.51494	1.90967	0.02444
C	-0.02828	2.36666	1.23832
C	-1.00499	3.36642	1.20595
C	-1.43331	3.90939	-0.00388
C	-0.88892	3.44646	-1.19989
C	0.08366	2.44229	-1.20369
C	0.39496	1.73986	2.54341
C	0.6063	1.87896	-2.50159
H	-2.06432	-2.80146	-1.06615
H	-2.09683	-2.97087	0.69597
H	-2.12429	-0.9104	2.16792
H	-2.12077	0.70268	1.43094
H	-2.07803	0.94777	-1.08288
H	-2.04703	-0.4919	-2.11615
H	-4.36951	-3.40201	-0.27834
H	-4.22074	-2.37448	1.9961
H	-5.64894	-1.78069	1.13623
H	-4.41776	0.10703	2.22798

H	-4.16534	1.55811	0.20659
H	-5.62343	0.5573	0.08435
H	-4.34038	0.5239	-2.0626
H	-4.13954	-1.95695	-2.30429
H	-5.60229	-1.53684	-1.40122
H	3.76041	-2.95547	-0.0792
H	6.24876	-2.68501	-0.08558
H	7.19482	-0.35301	-0.0112
H	5.60754	1.58192	0.0664
H	3.01149	2.00394	0.99326
H	3.03168	2.09742	-0.76271
H	-1.43874	3.71771	2.14138
H	-2.19469	4.6864	-0.01472
H	-1.23619	3.85563	-2.14777
H	1.47374	1.8439	2.71845
H	-0.12878	2.2012	3.38858
H	0.17794	0.66381	2.54402
H	1.69296	2.00113	-2.60107
H	0.4039	0.80167	-2.56186
H	0.13454	2.37016	-3.36036
C	1.38224	-2.05008	1.7512
H	1.67374	-3.05866	1.40442
H	2.21902	-1.64859	2.34043
H	0.50321	-2.15816	2.3946
C	1.33997	-1.9848	-1.76653
H	2.19933	-1.6084	-2.33898
H	1.57175	-3.02035	-1.45511
H	0.459	-2.02262	-2.41565
N	3.37504	-0.93278	-0.00496

Complex 7

V	0.30447	0.73405	-0.54961
F	3.42676	-0.69324	2.29373
F	4.35243	-0.24643	0.40114
F	4.43809	-2.25402	1.18329
F	3.55993	-1.75457	-1.66866
F	2.89865	-3.57141	-0.69438
F	1.48171	-2.31027	-1.73265
F	2.07286	-3.20617	2.0014
F	0.4223	-2.937	0.64333
F	0.79388	-1.47614	2.18586
O	1.77425	-0.28072	-0.00346

N	-1.01074	-0.1875	-0.42081
N	2.02943	2.2126	-0.80775
N	-0.34088	2.31494	0.23113
C	-2.21354	-0.96414	-0.49687
C	-1.98761	-2.16333	-1.44298
C	-2.60062	-1.47272	0.90694
C	-3.37077	-0.10593	-1.04721
C	-3.26757	-3.00774	-1.52229
C	-3.63292	-3.51596	-0.11889
C	-3.87721	-2.32084	0.81564
C	-5.0216	-1.45785	0.26307
C	-4.64911	-0.95194	-1.13895
C	-4.4153	-2.14879	-2.07247
C	3.20025	1.99356	-1.42034
C	4.19275	2.9581	-1.48596
C	3.96032	4.19327	-0.87743
C	2.75216	4.41278	-0.23049
C	1.8036	3.38778	-0.22046
C	0.47152	3.50118	0.45547
C	-1.66306	2.50097	0.74026
C	-1.98167	2.05819	2.03511
C	-3.28456	2.24613	2.50505
C	-4.24585	2.87522	1.71873
C	-3.91312	3.31606	0.44112
C	-2.62574	3.13021	-0.06957
C	-0.95294	1.34989	2.87452
C	-2.29927	3.51387	-1.4885
C	0.19129	0.87179	-2.59773
C	2.30422	-1.47125	0.34051
C	3.65934	-1.17356	1.06586
C	2.5668	-2.30355	-0.95315
C	1.38803	-2.28869	1.31024
H	0.63514	3.67179	1.53801
H	-0.047	4.40645	0.08888
H	2.53749	5.36104	0.26398
H	3.33164	0.99946	-1.84962
H	-0.76561	0.5753	-3.04485
H	0.96863	0.16289	-2.93747
H	0.46527	1.88313	-2.93396
H	4.72081	4.97529	-0.90535
H	5.13201	2.74319	-1.99446
H	-1.99622	2.62621	-2.06433

H	-1.46303	4.22706	-1.55115
H	-3.1688	3.97087	-1.98018
H	-5.25747	3.01945	2.10242
H	-3.54427	1.89474	3.50648
H	-1.32876	1.17296	3.89144
H	-0.01586	1.92159	2.94991
H	-0.69204	0.37927	2.42884
H	-4.53639	-4.14676	-0.16934
H	-2.81949	-4.14611	0.27783
H	-4.66977	3.79554	-0.18434
H	-1.14654	-2.76545	-1.07532
H	-1.70837	-1.78476	-2.4395
H	-3.09215	0.28904	-2.0378
H	-3.53367	0.75087	-0.37967
H	-5.46358	-0.32423	-1.53387
H	-3.09024	-3.86412	-2.19191
H	-1.77108	-2.06031	1.32427
H	-2.76459	-0.60577	1.5659
H	-5.33586	-2.75104	-2.15336
H	-4.17003	-1.79512	-3.08808
H	-4.13833	-2.68469	1.82193
H	-5.95364	-2.04596	0.21817
H	-5.20608	-0.60233	0.93421

Complex 8

V	-1.56099	0.00065	0.03636
Cl	-2.62586	0.60387	2.02126
Cl	-2.17683	-0.46785	-2.1564
N	0.04825	-0.10066	0.18857
N	-2.17448	-2.03213	0.56709
C	-1.38883	-3.1071	-0.05584
C	-3.61976	-2.2676	0.39978
N	-1.69126	2.09977	-0.57458
C	-0.95442	3.04695	0.27487
C	-3.07193	2.56312	-0.80249
H	-1.98067	-2.02366	1.5704
H	-1.23074	2.05001	-1.48561
H	-1.72246	-4.09973	0.29293
H	-0.32912	-2.96856	0.18492
H	-1.51021	-3.0445	-1.14553
H	-3.90939	-3.2566	0.79345
H	-4.17737	-1.48699	0.93293

H	-3.86185	-2.21825	-0.67027
H	-1.01043	4.07235	-0.12941
H	-1.38859	3.0271	1.28296
H	0.09473	2.73711	0.34531
H	-3.08448	3.58309	-1.22256
H	-3.60565	2.5609	0.15723
H	-3.5737	1.87798	-1.4972
C	2.07429	0.55065	1.39522
H	1.67448	1.57021	1.51751
H	1.74451	-0.02829	2.27294
C	3.60755	0.57968	1.3012
H	4.01689	1.03837	2.2149
C	1.4811	-0.08291	0.12066
C	1.92515	0.735	-1.1111
H	1.52916	1.76055	-1.02687
H	1.48373	0.28686	-2.01571
C	4.02945	1.40493	0.07516
H	5.12927	1.45444	0.01204
H	3.6657	2.44165	0.17469
C	3.45757	0.76561	-1.19991
H	3.75692	1.3574	-2.07939
C	3.98698	-0.66944	-1.33797
H	3.59289	-1.13061	-2.2588
H	5.08619	-0.66121	-1.4252
C	4.13967	-0.85459	1.16007
H	3.85932	-1.45074	2.04475
H	5.24128	-0.84655	1.11181
C	2.02851	-1.51835	-0.02033
H	1.70894	-2.11231	0.85249
H	1.59264	-1.98192	-0.92005
C	3.5621	-1.49258	-0.11237
H	3.93427	-2.52434	-0.21271

Complex 9

V	-0.36099	0.43382	-0.09107
Cl	-0.96059	0.59879	-2.3847
Cl	-0.86285	0.68658	2.24564
P	-2.9278	-0.47978	-0.05639
P	-1.71601	2.63925	-0.02069
N	1.13008	1.08848	-0.15561
N	0.13776	-1.29728	-0.00952
C	2.44457	1.50851	-0.20708

C	3.20872	1.22965	-1.36416
C	4.53815	1.64923	-1.3939
C	5.10361	2.32414	-0.31493
C	4.34203	2.58168	0.82152
C	3.00884	2.17757	0.90282
C	2.60391	0.4794	-2.51549
C	2.19838	2.43159	2.14074
C	0.59271	-2.46239	0.1579
C	0.58036	-3.43961	-1.04562
C	0.04537	-2.72236	-2.2911
C	1.99253	-3.95704	-1.38148
C	-0.37397	-4.60881	-0.73696
C	1.05204	-2.83643	1.60113
C	1.89017	-1.66992	2.15609
C	1.91184	-4.10267	1.73781
C	-0.22591	-3.00369	2.44567
C	-3.65326	-1.19592	1.47462
C	-3.53933	-1.64002	-1.34426
C	-3.98369	1.01863	-0.36614
C	-3.47644	2.24079	0.40488
C	-1.86122	3.64527	-1.55046
C	-1.27355	3.91749	1.21944
H	5.13843	1.44012	-2.28216
H	6.1452	2.64783	-0.35907
H	4.78899	3.10297	1.67092
H	1.7002	0.9761	-2.89447
H	3.32757	0.36938	-3.33444
H	2.28456	-0.52349	-2.19368
H	1.25237	2.93814	1.90721
H	1.91456	1.48827	2.62949
H	2.76154	3.04449	2.85755
H	0.69153	-1.88849	-2.59364
H	-0.01015	-3.43916	-3.12513
H	-0.95193	-2.29881	-2.12678
H	2.36188	-4.7061	-0.67269
H	1.97323	-4.42849	-2.37622
H	2.71751	-3.12883	-1.42119
H	-1.39446	-4.23657	-0.55476
H	-0.41354	-5.28751	-1.60369
H	-0.0708	-5.20223	0.13531
H	2.25813	-1.92734	3.1617
H	2.76208	-1.47138	1.51269

H	1.29837	-0.75114	2.23155
H	1.43206	-5.01239	1.35489
H	2.88957	-3.98785	1.24971
H	2.10356	-4.26816	2.80944
H	-0.81413	-2.07536	2.44073
H	-0.85091	-3.82945	2.06941
H	0.04195	-3.23277	3.48964
H	-4.73589	-1.36452	1.36925
H	-3.15487	-2.15415	1.68376
H	-3.45003	-0.52365	2.31896
H	-4.63791	-1.70878	-1.33709
H	-3.18935	-1.29207	-2.32588
H	-3.11779	-2.63828	-1.15702
H	-3.93623	1.20275	-1.45182
H	-5.03438	0.80171	-0.11358
H	-3.49489	2.05176	1.48994
H	-4.10696	3.12316	0.20857
H	-2.43489	4.56453	-1.3579
H	-0.8509	3.90488	-1.89779
H	-2.34046	3.05305	-2.33969
H	-1.14637	3.43986	2.19928
H	-0.32462	4.38601	0.92038
H	-2.05353	4.69183	1.27276

Complex 10

Ti	0.0214	-0.05716	-0.71265
C	0.17699	1.29016	1.20295
C	-1.10862	0.66929	1.21283
C	1.16013	0.26893	1.32473
C	-0.91675	-0.73557	1.33753
C	0.4867	-0.98693	1.3769
C	0.45838	2.76013	1.14374
C	-2.4341	1.36642	1.17604
C	2.63174	0.48853	1.48448
C	-2.00357	-1.75006	1.50947
C	1.14349	-2.3289	1.49644
H	2.86355	0.65248	2.54935
H	3.21139	-0.37602	1.13761
H	2.97542	1.36722	0.92292
H	2.10159	-2.35189	0.95974
H	1.34088	-2.56708	2.55355
H	0.51014	-3.12356	1.08057

H	-2.29006	-1.80259	2.57235
H	-2.899	-1.49073	0.92935
H	-1.67906	-2.74947	1.19401
H	-2.81357	1.51025	2.20045
H	-2.358	2.34958	0.6955
H	-3.18054	0.78265	0.62031
H	-0.3694	3.30973	0.67908
H	0.6093	3.15791	2.15991
H	1.36614	2.97115	0.56183
Cl	-1.03508	-1.8369	-1.56808
Cl	-0.88452	1.66965	-1.81619
Cl	2.07102	-0.223	-1.59978

Complex 11

Ti	1.13263	0.02686	-0.57303
C	1.76126	-1.1767	1.34559
C	2.96233	-0.64593	0.77954
C	0.9542	-0.0842	1.77212
C	2.88844	0.76646	0.83903
C	1.63817	1.11902	1.43683
C	1.47749	-2.63581	1.54475
C	4.13417	-1.44493	0.29962
C	-0.33488	-0.18162	2.52851
C	3.97294	1.7195	0.44322
C	1.195	2.51739	1.74793
O	-0.65119	0.00946	-0.63002
C	-1.93372	-0.01404	-0.19498
C	-2.59168	1.20778	0.02851
C	-2.54706	-1.25983	0.02367
C	-3.8598	-1.25743	0.49878
C	-3.90338	1.15458	0.505
C	-4.53314	-0.06369	0.74342
C	-1.79114	-2.53482	-0.29941
H	-4.36666	-2.20551	0.68425
C	-1.88819	2.51172	-0.29793
H	-4.44361	2.08318	0.69485
H	-5.55746	-0.08323	1.11935
C	-1.89297	-2.84023	-1.79991
H	-0.72821	-2.34677	-0.08591
C	-2.21834	-3.73735	0.54214
H	-2.19302	-3.51179	1.62028
H	-3.23662	-4.07587	0.29262

H	-1.54121	-4.58454	0.35452
H	-1.51835	-1.99745	-2.39836
H	-1.29587	-3.72875	-2.05782
H	-2.94105	-3.02928	-2.08376
H	-0.81744	2.36557	-0.09414
C	-2.01326	2.81395	-1.79737
C	-2.35725	3.69512	0.54831
H	-1.72077	4.57145	0.35256
H	-3.3925	3.988	0.31091
H	-2.30924	3.47143	1.6259
H	-1.45368	3.72584	-2.05763
H	-1.60888	1.98731	-2.39903
H	-3.06973	2.96173	-2.0744
H	-0.12902	-0.19593	3.61062
H	-1.00129	0.66567	2.32153
H	-0.89084	-1.09459	2.27907
H	0.13366	2.55465	2.02495
H	1.77514	2.9186	2.59411
H	1.34435	3.18829	0.88973
H	4.70868	1.80654	1.25926
H	4.50406	1.37983	-0.45616
H	3.57257	2.71938	0.23473
H	4.87942	-1.53879	1.10627
H	3.83421	-2.45424	-0.00886
H	4.62554	-0.96724	-0.559
H	1.63403	-3.20495	0.61738
H	2.15138	-3.04853	2.31212
H	0.44646	-2.80794	1.87889
Cl	1.62879	1.8412	-1.83543
Cl	1.67607	-1.72074	-1.91082

Complex 12

Ti	1.19564	-0.02744	0.75868
C	2.52317	1.17008	-0.81111
C	3.30222	0.07189	-0.34867
C	1.39195	0.64149	-1.49702
C	2.66212	-1.13179	-0.75613
C	1.47456	-0.77688	-1.45746
C	2.87756	2.62206	-0.69913
C	4.58931	0.15044	0.41649
C	0.34605	1.41809	-2.24138
C	3.21447	-2.51473	-0.59517

C	0.51622	-1.71367	-2.13185
O	-0.61461	-0.01422	0.78081
C	-1.84775	0.01132	0.23755
C	-2.49517	-1.20794	-0.0362
C	-2.44439	1.25735	-0.03384
C	-3.71189	1.25744	-0.6193
C	-3.76132	-1.15406	-0.62311
C	-4.3657	0.06481	-0.91843
C	-1.71354	2.52894	0.35933
H	-4.20092	2.2055	-0.84805
C	-1.82596	-2.5097	0.3679
H	-4.28814	-2.08129	-0.85393
H	-5.35398	0.08614	-1.38057
C	-1.86498	2.78117	1.86582
H	-0.64233	2.35561	0.17029
C	-2.12873	3.7571	-0.44965
H	-2.05042	3.57507	-1.53263
H	-3.16463	4.06223	-0.23086
H	-1.48077	4.61081	-0.19773
H	-1.50875	1.91733	2.44545
H	-1.28339	3.66421	2.17562
H	-2.92201	2.95689	2.12275
H	-0.74469	-2.37765	0.21113
C	-2.03016	-2.76356	1.86785
C	-2.26604	-3.71547	-0.46145
H	-1.66088	-4.59645	-0.19696
H	-3.31931	-3.98013	-0.27556
H	-2.14751	-3.5304	-1.54026
H	-1.48942	-3.66817	2.18879
H	-1.66052	-1.91571	2.46269
H	-3.09961	-2.90257	2.09429
H	0.5476	1.38313	-3.32435
H	-0.66281	1.01102	-2.08032
H	0.3317	2.47544	-1.94513
H	-0.52228	-1.36048	-2.05011
H	0.75308	-1.80064	-3.2048
H	0.56228	-2.72392	-1.70249
H	3.85304	-2.77369	-1.45527
H	3.82651	-2.60549	0.31228
H	2.41858	-3.26984	-0.53372
H	5.45108	-0.03597	-0.24437
H	4.72872	1.13935	0.87326

H	4.62552	-0.59665	1.22323
H	3.46404	2.83182	0.20522
H	3.47507	2.94104	-1.56827
H	1.98051	3.25648	-0.66209
C	1.67181	1.55314	2.04222
H	2.7457	1.65724	2.26517
H	1.29426	2.52163	1.67355
H	1.13903	1.32087	2.98234
C	1.643	-1.66103	1.98401
H	2.70924	-1.76115	2.24261
H	1.07391	-1.47526	2.91307
H	1.29428	-2.61791	1.56048