The Chlorinating Behaviour of WCl_6 Towards α-Aminoacids

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Figure S1. DFT-calculated structure of $[\overline{NH_2(CH_2)_3}CHC(O)Cl][WOCl_5]$, **1a**, with implicit solvation (G = –3229.7021 a.u.).

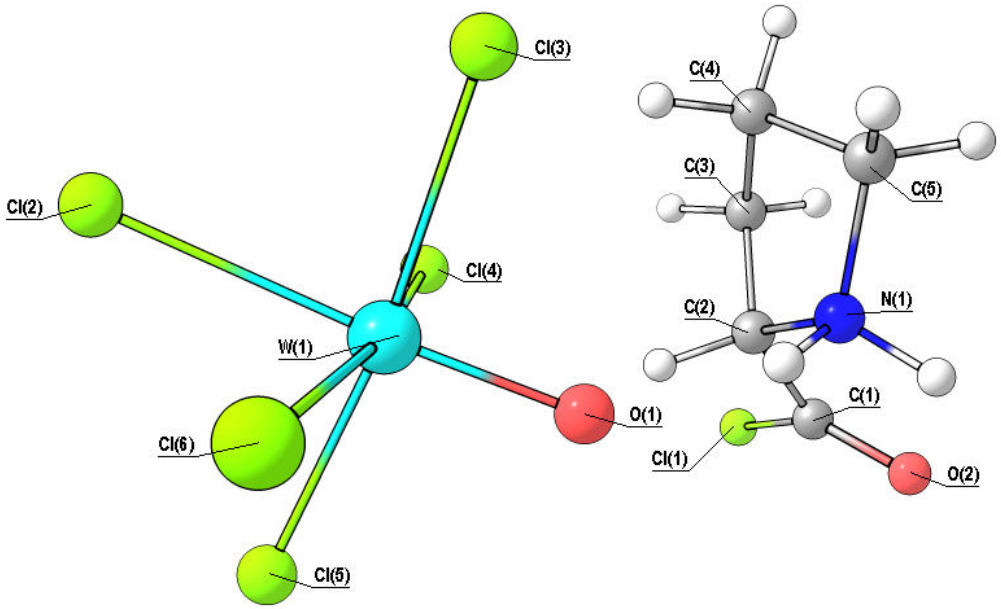

Table S1. Selected computed bond distances (Å) and angles (°) for $[\overline{NH_2(CH_2)_3}CHC(O)Cl][WOCl_5]$, **1a**.

	M06/C-PCM
W(1)–O(1)	1.689
W(1)–Cl(2)	2.459
W(1)–Cl(3)	2.356
W(1)–Cl(4)	2.370
W(1)–Cl(5)	2.321
W(1)–Cl(6)	2.317
O(1)---N(1)	2.844
C(1)–O(2)	1.192
C(1)–Cl(1)	1.764
O(1)–W(1)–Cl(2)	176.3
O(1)–W(1)–Cl(3)	91.8
O(1)–W(1)–Cl(4)	91.7
O(1)–W(1)–Cl(5)	95.2
O(1)–W(1)–Cl(6)	95.3

Figure S2. DFT-calculated structure of $[MeNH_2CH_2C(O)Cl][WOCl_5]$, **1b**, with implicit solvation (G = −3152.4020 a.u.).

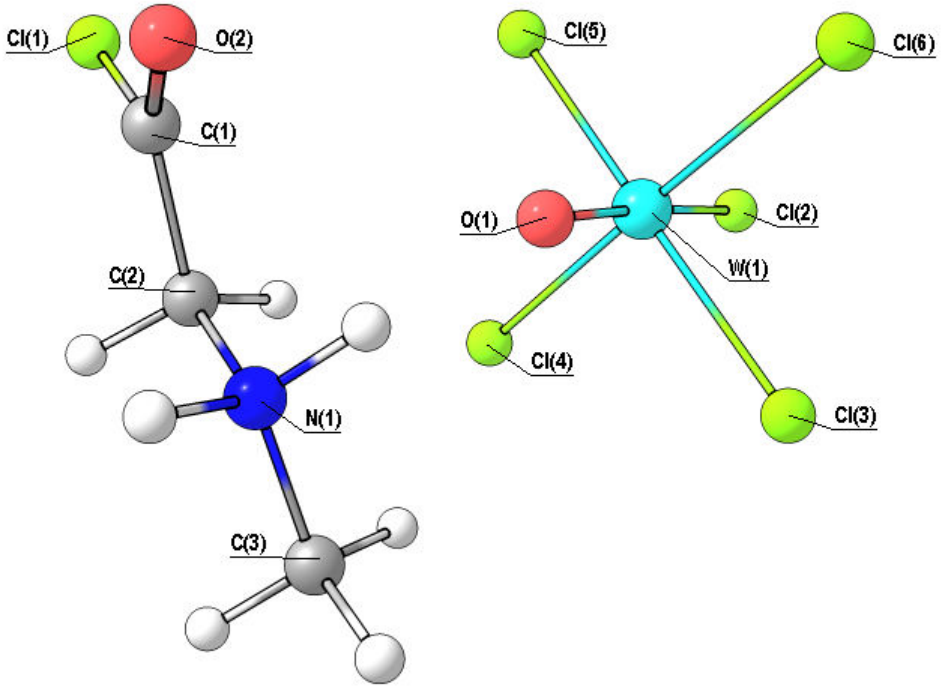

Table S2. Selected computed bond distances (Å) and angles (°) for $[MeNH_2CH_2C(O)Cl][WOCl_5]$, **1b**.

	M06/C-PCM
W(1)–O(1)	1.689
W(1)–Cl(2)	2.458
W(1)–Cl(3)	2.336
W(1)–Cl(4)	2.385
W(1)–Cl(5)	2.330
W(1)–Cl(6)	2.311
O(1)---N(1)	2.779
C(1)–O(2)	1.190
C(1)–Cl(1)	1.767
O(1)–W(1)–Cl(2)	176.1
O(1)–W(1)–Cl(3)	93.0
O(1)–W(1)–Cl(4)	91.1
O(1)–W(1)–Cl(5)	94.2
O(1)–W(1)–Cl(6)	95.9

Figure S3. DFT-calculated structure of $[NH_3CH_2C(O)Cl][WOCl_5]$, **1c**, with implicit solvation (G = –3113.1827 a.u.).

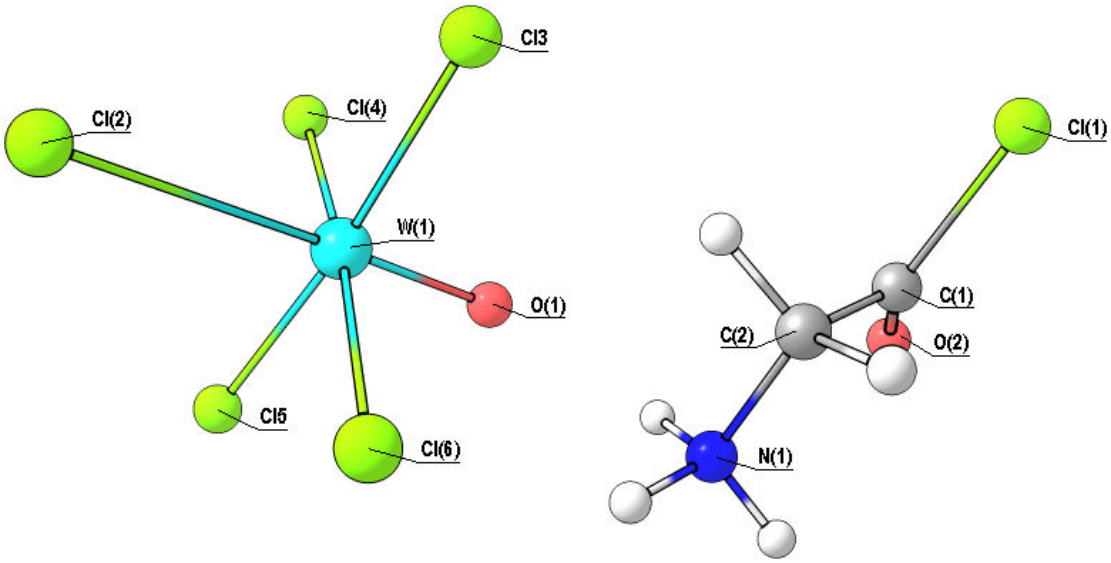

Table S3. Selected computed bond distances (Å) and angles (°) for $[NH_3CH_2C(O)Cl][WOCl_5]$, **1c**.

	M06/C-PCM
W(1)–O(1)	1.686
W(1)–Cl(2)	2.449
W(1)–Cl(3)	2.356
W(1)–Cl(4)	2.422
W(1)–Cl(5)	2.315
W(1)–Cl(6)	2.296
O(1)---N(1)	2.783
C(1)–O(2)	1.189
C(1)–Cl(1)	1.768
O(1)–W(1)–Cl(2)	173.3
O(1)–W(1)–Cl(3)	92.0
O(1)–W(1)–Cl(4)	97.2
O(1)–W(1)–Cl(5)	95.0
O(1)–W(1)–Cl(6)	89.2

Figure S4. DFT-calculated structure of $[NH_3CH(CH_3)C(O)Cl][WOCl_5]$, **1d**, with implicit solvation (G = −3152.4147 a.u.).

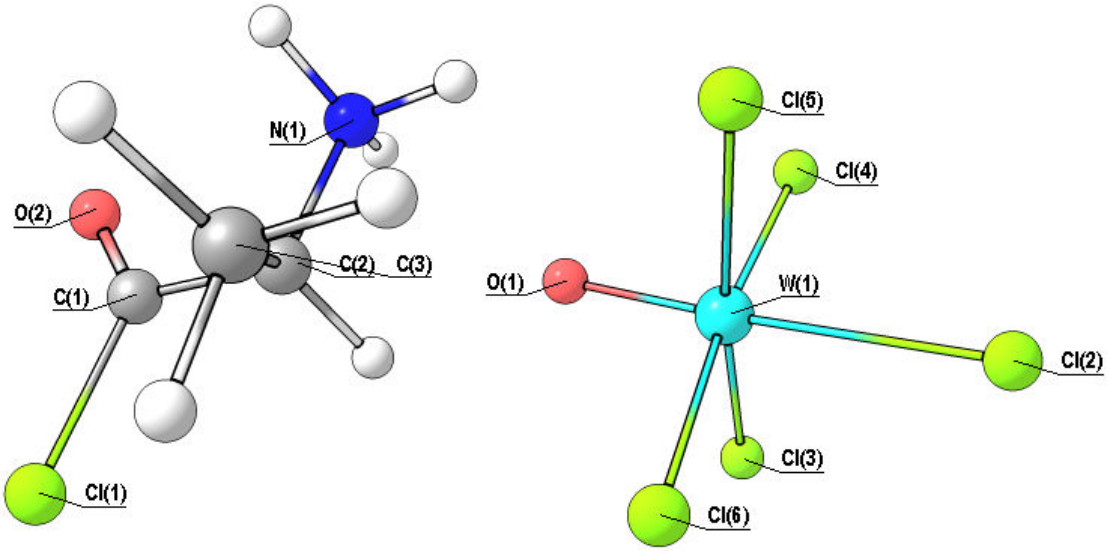

Table S4. Selected computed bond distances (Å) and angles (°) for $[NH_3CH(CH_3)C(O)Cl][WOCl_5]$, **1d**.

	M06/C-PCM
W(1)–O(1)	1.684
W(1)–Cl(2)	2.452
W(1)–Cl(3)	2.294
W(1)–Cl(4)	2.315
W(1)–Cl(5)	2.432
W(1)–Cl(6)	2.353
O(1)---N(1)	2.806
C(1)–O(2)	1.190
C(1)–Cl(1)	1.769
O(1)–W(1)–Cl(2)	172.9
O(1)–W(1)–Cl(3)	97.4
O(1)–W(1)–Cl(4)	95.0
O(1)–W(1)–Cl(5)	89.0
O(1)–W(1)–Cl(6)	92.0

Figure S5. DFT-calculated structure of $WCl_6[O{=}C(O)\overline{CH(CH_2)_3NH_2}]$, **3**, with implicit solvation (G = –3229.6439 a.u.).

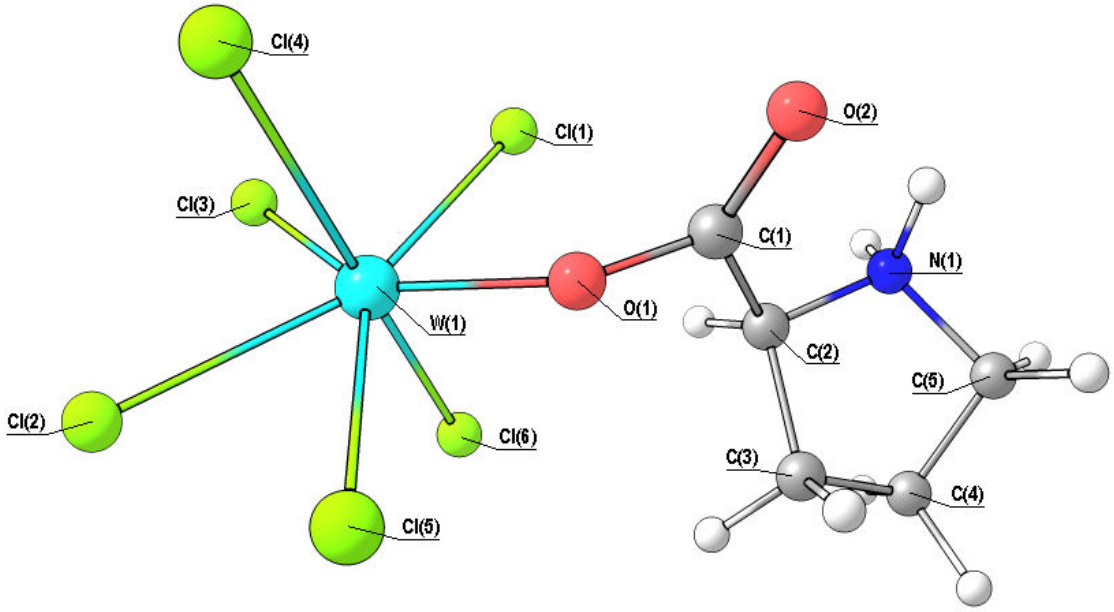

Table S5. Selected computed bond distances (Å) and angles (°) for $WCl_6[O{=}C(O)\overline{CH(CH_2)_3NH_2}]$, **3**.

	EDF2	**M06/C-PCM**
W(1)–Cl(1)	2.480	2.478
W(1)–Cl(2)	2.397	2.425
W(1)–Cl(3)	2.402	2.427
W(1)–Cl(4)	2.279	2.284
W(1)–Cl(5)	2.425	2.442
W(1)–Cl(6)	2.345	2.311
W(1)–O(1)	2.004	1.952
O(2)···N(1)	2.670	2.656
C(1)–O(1)	1.300	1.315
C(1)–O(2)	1.216	1.210
O(1)–W(1)–Cl(1)	71.9	72.6
O(1)–W(1)–Cl(2)	142.6	142.8
O(1)–W(1)–Cl(3)	143.5	144.6
O(1)–W(1)–Cl(4)	88.4	90.8
O(1)–W(1)–Cl(5)	70.2	70.1
O(1)–W(1)–Cl(6)	87.8	90.4
W(1)–O(1)–C(1)	140.9	144.4

Figure S6. DFT-calculated structure of $WCl_5[OC(Cl)(OH)CH(CH_2)_3NH]$, **4**, with implicit solvation (G = −3229.6432 a.u.).

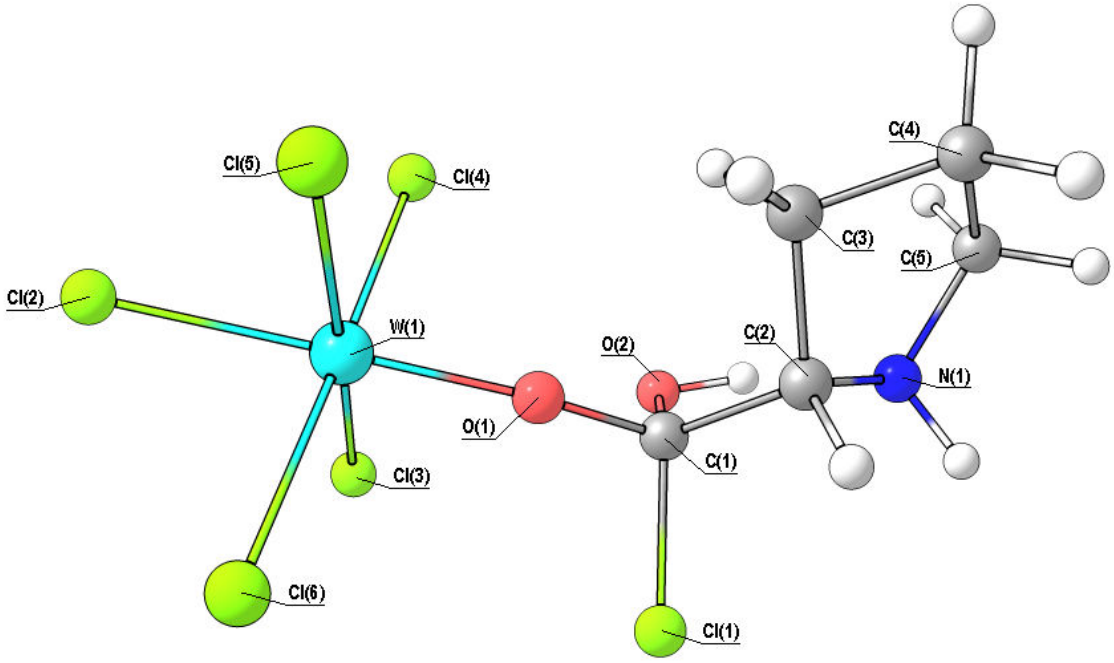

Table S6. Selected computed bond distances (Å) and angles (°) for $WCl_5[OC(Cl)(OH)CH(CH_2)_3NH]$, **4**.

	EDF2	**M06/C-CPM**
W(1)–O(1)	1.840	1.809
W(1)–Cl(2)	2.314	2.317
W(1)–Cl(3)	2.341	2.313
W(1)–Cl(4)	2.344	2.313
W(1)–Cl(5)	2.321	2.304
W(1)–Cl(6)	2.316	2.302
C(1)–O(1)	1.379	1.390
C(1)–O(2)	1.337	1.332
C(1)–Cl(1)	1.870	1.865
O(2)···N(1)	2.581	2.582
O(1)–W(1)–Cl(2)	178.4	176.3
O(1)–W(1)–Cl(3)	89.7	88.8
O(1)–W(1)–Cl(4)	90.3	89.6
O(1)–W(1)–Cl(5)	91.4	92.9
O(1)–W(1)–Cl(6)	90.7	91.5
W(1)–O(1)–C(1)	167.8	157.9

Figure S7. DFT-calculated structure of $WOCl_4[O=C(Cl)\overline{CH(CH_2)_3NH}]$, **5a**, with implicit solvation ($G_{\mathbf{5a}+HCl}$ = −3229.6887 a.u.).

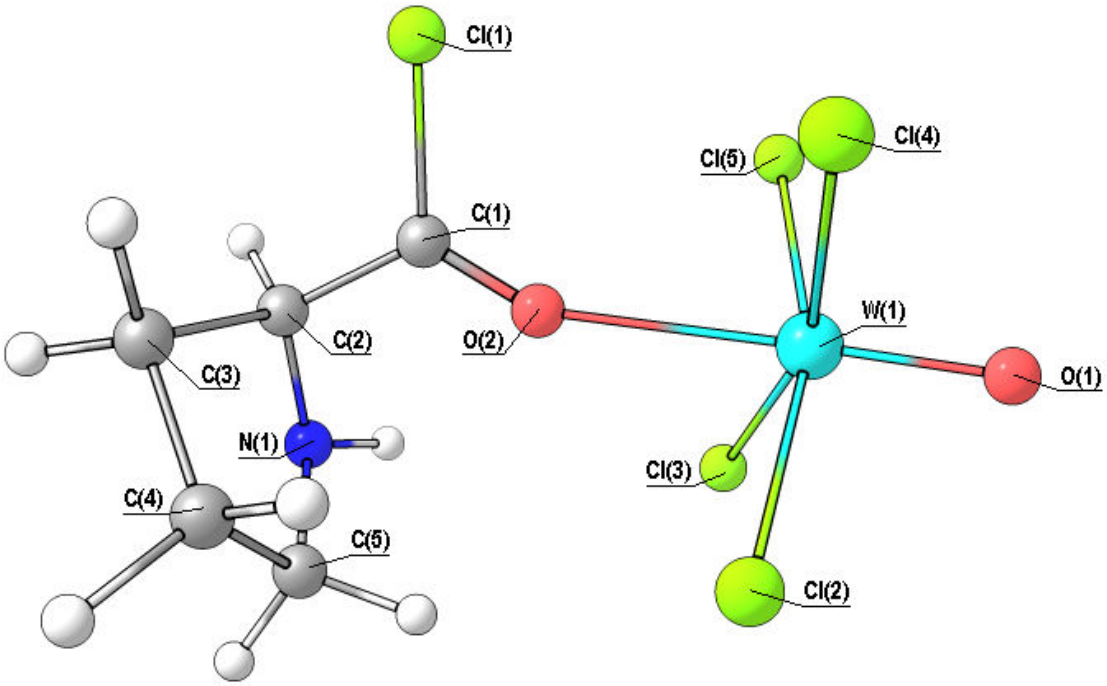

Table S7. Selected computed bond distances (Å) and angles (°) for $WOCl_4[O=C(Cl)\overline{CH(CH_2)_3NH}]$, **5a**.

	EDF2	**M06/C-PCM**
W(1)–O(1)	1.679	1.655
W(1)–Cl(2)	2.339	2.317
W(1)–Cl(3)	2.332	2.315
W(1)–Cl(4)	2.323	2.311
W(1)–Cl(5)	2.320	2.310
W(1)–O(2)	2.403	2.364
C(1)–O(2)	1.203	1.206
C(1)–Cl(1)	1.771	1.762
O(2)···N(1)	2.793	2.790
O(1)–W(1)–O(2)	177.4	178.5
O(1)–W(1)–Cl(2)	99.5	99.3
O(1)–W(1)–Cl(3)	98.7	99.1
O(1)–W(1)–Cl(4)	99.5	99.1
O(1)–W(1)–Cl(5)	99.7	99.8
W(1)–O(2)–C(1)	157.6	155.9

Figure S8. DFT-calculated structure of $WOCl_4[O=C(Cl)CH_2NHMe]$, **5b**, with implicit solvation ($G_{\mathbf{5b}+HCl}$ = −3152.3936 a.u.).

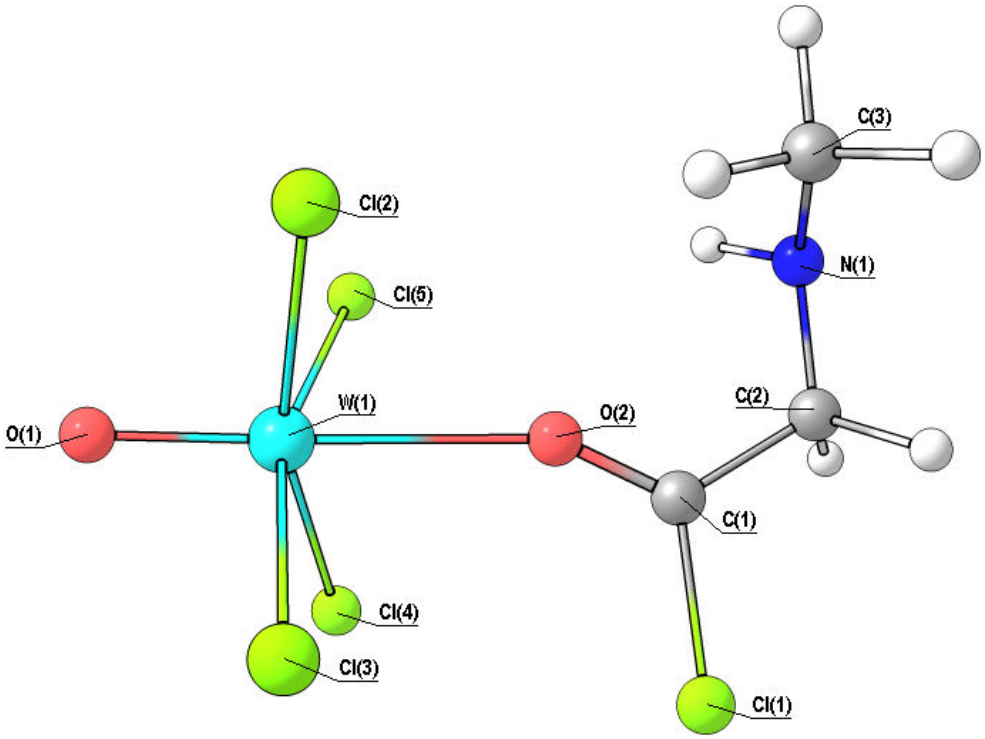

Table S8. Selected computed bond distances (Å) and angles (°) for $WOCl_4[O=C(Cl)CH_2NHMe]$, **5b**.

	EDF2	**M06/C-PCM**
W(1)–O(1)	1.679	1.654
W(1)–Cl(2)	2.330	2.315
W(1)–Cl(3)	2.330	2.315
W(1)–Cl(4)	2.320	2.311
W(1)–Cl(5)	2.321	2.311
W(1)–O(2)	2.474	2.381
C(1)–O(2)	1.203	1.205
C(1)–Cl(1)	1.770	1.762
O(1)–W(1)–O(2)	178.3	178.5
O(1)–W(1)–Cl(2)	100.1	99.2
O(1)–W(1)–Cl(3)	99.5	99.1
O(1)–W(1)–Cl(4)	99.3	98.8
O(1)–W(1)–Cl(5)	100.1	99.3
W(1)–O(2)–C(1)	150.7	154.2

Figure S9. DFT-calculated structure of $WOCl_4[O=C(Cl)CH_2NH_2]$, **5c**, with implicit solvation ($G_{\mathbf{5c}+HCl}$ = –3113.1763 a.u.).

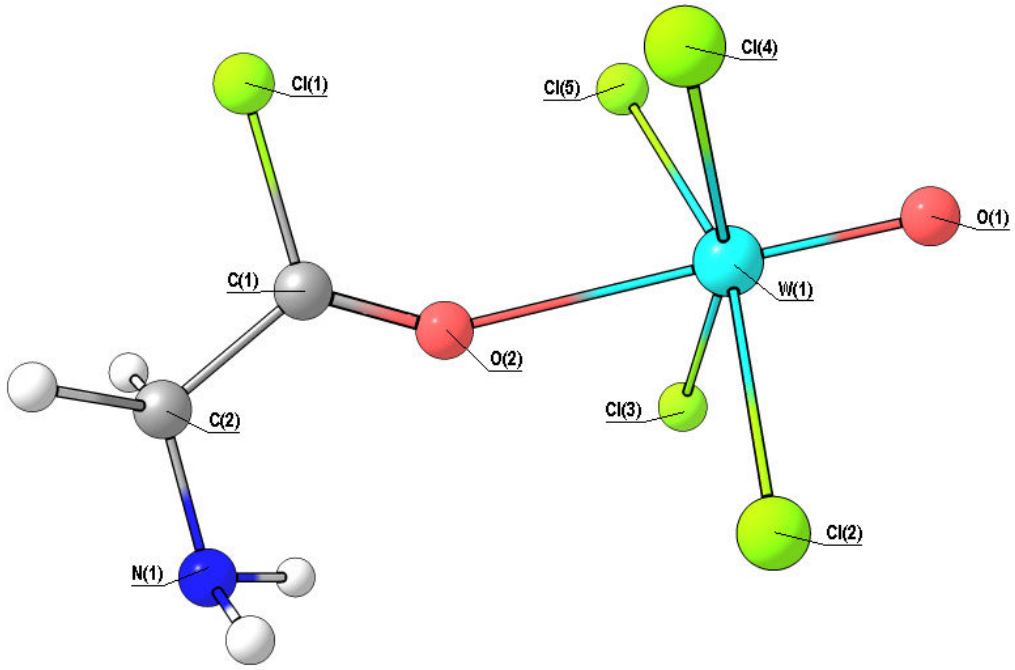

Table S9. Selected computed bond distances (Å) and angles (°) for $WOCl_4[O=C(Cl)CH_2NH_2]$, **5c**.

	EDF2	**M06/C-PCM**
W(1)–O(1)	1.679	1.655
W(1)–Cl(2)	2.330	2.316
W(1)–Cl(3)	2.330	2.312
W(1)–Cl(4)	2.321	2.312
W(1)–Cl(5)	2.320	2.308
W(1)–O(2)	2.474	2.389
C(1)–O(2)	1.203	1.206
C(1)–Cl(1)	1.770	1.757
O(1)–W(1)–O(2)	178.3	178.8
O(1)–W(1)–Cl(2)	100.1	99.2
O(1)–W(1)–Cl(3)	100.1	99.6
O(1)–W(1)–Cl(4)	99.3	99.0
O(1)–W(1)–Cl(5)	99.5	99.0
W(1)–O(2)–C(1)	150.7	150.5

Figure S10. DFT-calculated structure of $WOCl_4[O=C(Cl)CH(CH_3)NH_2]$, **5d**, with implicit solvation ($G_{\mathbf{5d}+HCl}$ = −3152.4082 a.u.).

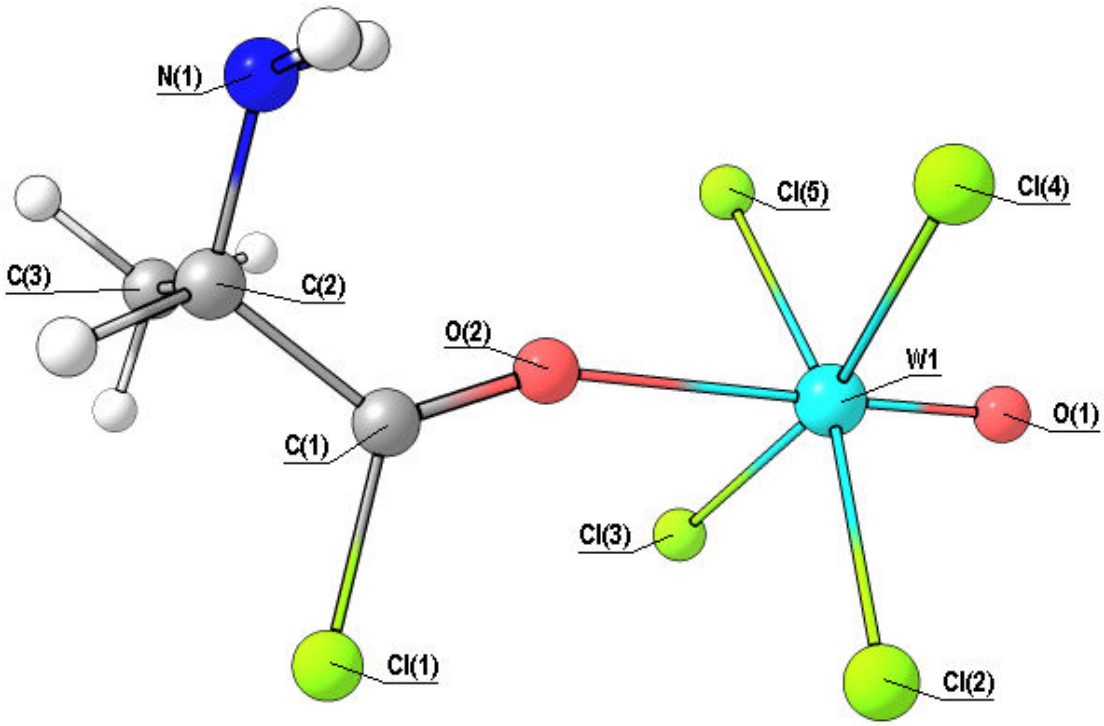

Table S10. Selected computed bond distances (Å) and angles (°) for $WOCl_4[O=C(Cl)CH(CH_3)NH_2]$, **5d**.

	EDF2	**M06/C-PCM**
W(1)–O(1)	1.680	1.654
W(1)–Cl(2)	2.319	2.311
W(1)–Cl(3)	2.324	2.312
W(1)–Cl(4)	2.329	2.315
W(1)–Cl(5)	2.335	2.316
W(1)–O(2)	2.427	2.363
C(1)–O(2)	1.204	1.205
C(1)–Cl(1)	1.767	1.759
O(1)–W(1)–O(2)	177.8	178.9
O(1)–W(1)–Cl(2)	99.3	98.5
O(1)–W(1)–Cl(3)	99.7	99.2
O(1)–W(1)–Cl(4)	99.7	99.5
O(1)–W(1)–Cl(5)	99.5	99.1
W(1)–O(2)–C(1)	153.9	156.2

Figure S11. DFT-calculated structure of {$WOCl_4$[O=C(Cl)$\overline{CH(CH_2)_3NH_2}$]}Cl, **6**, with implicit solvation (G = –3229.6886 a.u.).

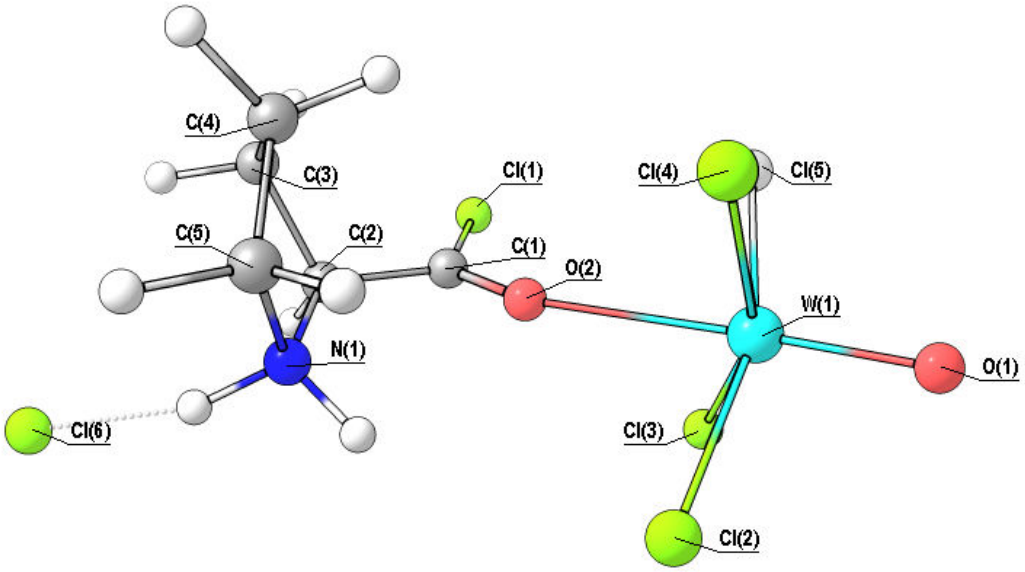

Table S11. Selected computed bond distances (Å) and angles (°) for {$WOCl_4$[O=C(Cl)$\overline{CH(CH_2)_3NH_2}$]}Cl, **6**.

	EDF2	**M06/C-PCM**
W(1)–O(1)	1.677	1.652
W(1)–Cl(2)	2.349	2.320
W(1)–Cl(3)	2.311	2.304
W(1)–Cl(4)	2.331	2.315
W(1)–Cl(5)	2.314	2.304
W(1)–O(2)	2.474	2.430
C(1)–O(2)	1.202	1.207
C(1)–Cl(1)	1.758	1.729
O(2)···N(1)	2.742	2.665
O(1)–W(1)–O(2)	177.5	177.4
O(1)–W(1)–Cl(2)	98.8	98.9
O(1)–W(1)–Cl(3)	100.6	100.4
O(1)–W(1)–Cl(4)	100.7	100.6
O(1)–W(1)–Cl(5)	99.8	99.2
W(1)–O(2)–C(1)	168.2	156.5
Cl(6)···N(1)	2.865	2.952

Figure S12. DFT-calculated structure of **7**, with implicit solvation

($G_{7+⅔\ HCl}$ = −3229.7191 a.u.).

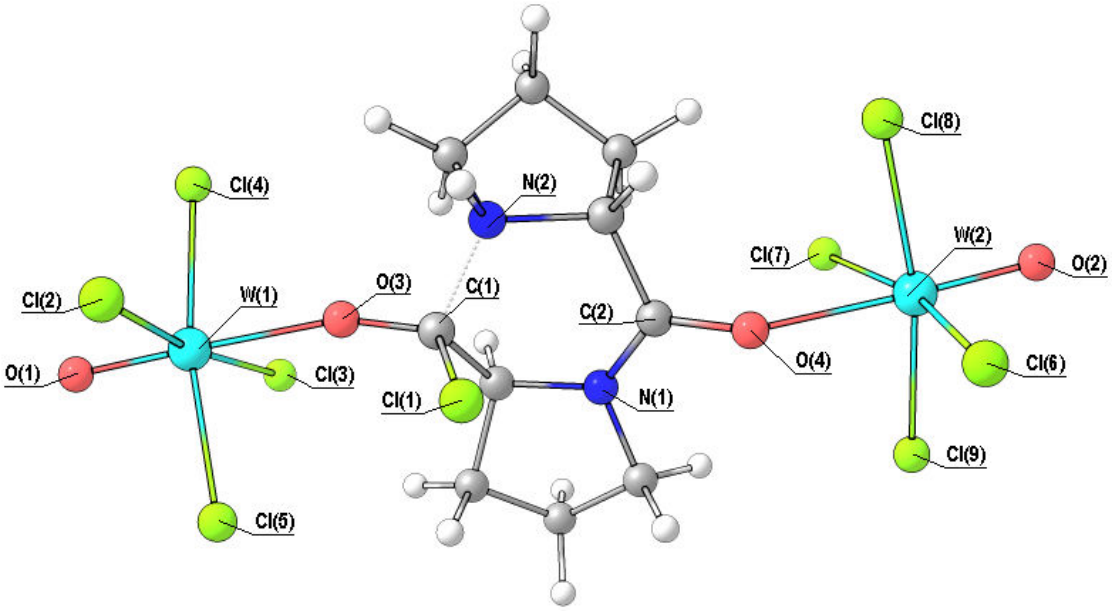

Table S12. Selected computed bond distances (Å) and angles (°) for **7**.

	M06/C-PCM
W(1)–O(1)	1.664
W(2)–O(2)	1.660
W(1)–Cl(2)	2.329
W(1)–Cl(3)	2.347
W(1)–Cl(4)	2.343
W(1)–Cl(5)	2.330
W(2)–Cl(6)	2.312
W(2)–Cl(7)	2.332
W(2)–Cl(8)	2.343
W(2)–Cl(9)	2.325
W(1)–O(3)	2.112
W(2)–O(4)	2.193
C(1)–O(3)	1.275
C(2)–O(4)	1.251
C(1)–Cl(1)	1.884
C(1)···N(2)	1.572