Synthesis and Properties of Oxygen-Centered Tetradecaimido Hexatantalum Clusters

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Supporting Information

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I. Additional Experimental Details

General. All manipulations were performed using standard Schlenk-line techniques or an N_2-atmosphere glovebox. Reactions followed by NMR spectroscopy were performed in 5 mm Pyrex NMR tubes which were flame-sealed under reduced pressure. Solvents were dried by passage through a column of activated alumina,[1] degassed with nitrogen and stored over 4 Å molecular sieves. Solvents were tested with Na/benzophenone prior to use. Deuterated solvents were vacuum-transferred from Na/benzophenone and stored in Teflon-sealed Kontes vessels inside a glovebox. NMR spectra were obtained with Bruker a DRX-500 spectrometer. Chemical shifts were calibrated relative to residual solvent peaks and are reported relative to TMS. UV-visible absorption spectra were recorded in THF on a Hewlett Packard 8453 spectrophotometer using a 2 mm path-length cell. Elemental analyses were performed at the UC, Berkeley Microanalytical Facility with a Perkin Elmer 2400 Series II CHNO/S Analyzer. Electrospray mass spectrometry was performed by Dr. John Greaves (using THF as the matrix) at the UC, Irvine Mass Spectrometry Facility. All starting

materials obtained from commercial sources were used without further purification, except *t*BuNH$_2$, pyridine, aniline and *m*-chloroaniline which were distilled prior to use. [Bn$_3$Ta=N-*t*Bu] was prepared as previously reported.[2] Isotopically-enriched water (30% ^{17}O, 50% ^{18}O) was purchased from Isotec and degassed prior to use.

General procedure for preparation of (ArN)$_{14}$Ta$_6$O. Compound **1** (100 mg, 0.190 mmol, 1 equiv) was dissolved in 1 mL of benzene. The aniline (0.950 mmol, 5 equiv) was treated with 0.6 μL (0.03 mmol, 0.16 equiv) of degassed water via microsyringe and then dissolved in 0.5 mL benzene. The two solutions were mixed, and the reaction mixture was transferred to a Kontes reaction vessel. Hexane (4 mL) was then added, causing the formation of a yellow precipitate. The vessel was sealed with a Teflon valve and immersed in a 135 °C oil bath. After a few minutes, most of the yellow solid had dissolved and the solution had developed a red color. After heating for ca. 24 h the reaction vessel was allowed to cool and was transferred to a glove box. The supernatant was removed and the crystalline product was washed with Et$_2$O (2 x 2 mL) then pentane (2 x 2 mL). Isotopically-enriched samples were prepared in an identical fashion using ^{17}O/^{18}O enriched water.

Reaction conditions from which crystals of 5 were obtained. Compound **1** (10.0 mg, 0.019 mmol, 1 equiv) was dissolved in 0.6 mL of C$_6$D$_6$, and the solution was added to 13.5 mg (0.106 mmol, 5.56 equiv) of *m*-chloroaniline. The reaction mixture was then transferred to an NMR tube that contained trace tantalum oxide from previous experiments. The NMR tube was flame sealed under reduced pressure and heated at 135 °C in an oil bath for 24 h. The reaction mixture was then allowed to stand at ambient temperature for ca. three weeks during which time red/orange crystals of **5** formed.

General procedure for reactivity studies. Compound **3** (5 mg, 0.002 mmol) was dissolved in 0.6 mL of C_6D_6 and the appropriate reagent was added via microsyringe. The reaction mixture was then transferred to an NMR tube and flame sealed under reduced pressure. The tube was then heated at 135 °C in an oil bath and the reaction was periodically monitored by NMR.

II. X-Ray Crystallography

General Procedures. A crystal of appropriate size was mounted on a Kaptan© loop using Paratone-N hydrocarbon oil. The crystal was transferred to a diffractometer/CCD area detector, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected and the raw data were integrated using SAINT.[3] Cell dimensions reported were calculated from all reflections with $I > 10\ \sigma$. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Data were analyzed for agreement and possible absorption using XPREP.[4] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[5] The structure was solved via direct methods, expanded using Fourier techniques, and refined on F^2 with the SHELXTL-97 suite of programs.[6] ORTEP diagrams were created using the ORTEP-3 software package[7] and rendered using the POV-ray graphics program.[8]

III. Computational Methods

Molecular orbital calculations on **2** were performed using the Jaguar 6.5 package[9] with Maestro 7.5 as the graphical user interface[10] at the UC, Berkeley Molecular Graphics Facility. The initial

atomic coordinates were taken from the X-ray structural data. The hybrid DFT functional X3LYP[11] was used throughout, which consists of the Becke three-parameter functional[12] and the correlation functional of Lee, Yang and Par.[13] It also includes the Perdew-Wang 1991 gradient exchange functional[14] and the exchange has been parameterized to fit the Gaussian exchange density. We found that for this system the X3LYP functional gives results comparable to the well known B3LYP[15] but at slightly less computational cost. The LACVP* basis set was employed, which uses an effective core potential and valence double-ζ contraction basis functions for metals.[16] The remaining atoms were treated with Pople's 6-31G* basis set, which includes a set of d polarization functions for non-hydrogen atoms.[17] Single point energy calculations starting with the neutral cluster produced excited-state electronic configurations. Thus, the wavefunction was obtained by first calculating that of the dication using a level shift of 0.5 a.u. This wavefunction was then used as an initial guess for optimization of the neutral structure (level shift constraint removed). Vibrational frequency calculations performed on the resulting structure (same level of theory) confirmed that it was a true energetic minimum. Graphical representations of MOs were generated in and exported from Maestro.

Coordinates (Å) for C_i-Opimized 2.

atom	x	y	z
Ta1	1.2792696352	-0.9206652122	1.5736753355
Ta2	0.2060455097	1.9833567331	0.9806115666
Ta3	-1.8088255836	-0.4273567693	1.2170053725
N4	-0.2040941221	0.3947175746	2.4764755010
N5	2.1754757491	0.9094017597	0.9059241824
N6	2.2907007824	-1.7218594681	2.8117794926
N7	0.4349557612	3.5725637237	1.7644629300
N8	0.5451980369	2.1728011567	-1.1670576029
N9	-1.8508676926	1.6652733032	0.4382430588
N10	-3.2941999681	-0.7575413702	2.1549412685
O11	0.0000000000	0.0000000000	0.0000000000

C12	-0.3062871444	0.7738951731	3.8509594451
C13	0.7982117100	0.6975878133	4.7146509825
H14	1.7487380385	0.3329557894	4.3380206048
C15	0.6861467758	1.0856675521	6.0489282211
H16	1.5565348238	1.0105929950	6.6964596374
C17	-0.5230054332	1.5674451770	6.5513229655
H18	-0.6061463528	1.8692141749	7.5919932134
C19	-1.6216129163	1.6626984342	5.6962225772
H20	-2.5705871049	2.0455939134	6.0638198440
C21	-1.5163698765	1.2737750666	4.3625989213
H22	-2.3787306584	1.3578790516	3.7077467258
C23	3.3839518773	1.5489229644	1.3310008455
C24	4.3019630879	0.9132659800	2.1815829369
H25	4.0988800787	-0.0929828892	2.5309936314
C26	5.4657948124	1.5674003389	2.5856698607
H27	6.1593325682	1.0528327128	3.2466535929
C28	5.7402394683	2.8654008537	2.1567583228
H29	6.6460959722	3.3727311947	2.4778794453
C30	4.8338990441	3.5045216495	1.3094739761
H31	5.0262588954	4.5170890200	0.9635752055
C32	3.6726100149	2.8559801355	0.8989428824
H33	2.9783068384	3.3690053734	0.2399955124
C34	3.0569554648	-2.3803015742	3.7516277150
C35	4.2951920193	-2.9444952228	3.3910477652
H36	4.6282923767	-2.8686315786	2.3596113537
C37	5.0700778343	-3.5951596980	4.3472031878
H38	6.0246605740	-4.0275181075	4.0564825047
C39	4.6311908977	-3.6947605645	5.6685268003
H40	5.2411757176	-4.2031751518	6.4107669471
C41	3.4021638230	-3.1391745765	6.0298891889
H42	3.0510158658	-3.2145534868	7.0562429247
C43	2.6168210874	-2.4863278021	5.0845978931
H44	1.6605423803	-2.0499206476	5.3578098065
C45	0.6491723913	4.7863049571	2.3834555104
C46	0.7431947644	5.9651546566	1.6200170167
H47	0.6490699902	5.9004242857	0.5391929943
C48	0.9506041688	7.1895060768	2.2496777296
H49	1.0231660679	8.0935833490	1.6494258518
C50	1.0663872218	7.2599938203	3.6386096808
H51	1.2261181260	8.2185013233	4.1258951549
C52	0.9751014252	6.0918252296	4.3989783779
H53	1.0652012493	6.1393660934	5.4815205488
C54	0.7690390183	4.8609336310	3.7837549305
H55	0.6948227073	3.9473484965	4.3672507794
C56	0.7186345497	3.4399131000	-1.8123031319
C57	1.9254936414	3.7924316562	-2.4346555162

H58	2.7548577550	3.0947597270	-2.4250511781
C59	2.0609881124	5.0244860718	-3.0733444452
H60	3.0063202604	5.2710094035	-3.5507718031
C61	1.0008456398	5.9289233304	-3.1103043883
H62	1.1087808696	6.8852122459	-3.6151072141
C63	-0.2034768238	5.5872032378	-2.4929222996
H64	-1.0449730680	6.2754811199	-2.5129490319
C65	-0.3439107105	4.3607841811	-1.8482428344
H66	-1.2889628253	4.1095520007	-1.3749971050
C67	-2.9902567402	2.5058245121	0.6455141426
C68	-2.8627514971	3.8296224671	1.0935170180
H69	-1.8764007026	4.2320602240	1.2961121547
C70	-3.9926545593	4.6198649153	1.3019284241
H71	-3.8652547684	5.6405359319	1.6546581610
C72	-5.2709152896	4.1135557050	1.0709336278
H73	-6.1481109650	4.7317385106	1.2421074862
C74	-5.4077939045	2.8006042713	0.6171758900
H75	-6.3950464000	2.3835907340	0.4330563041
C76	-4.2835951241	2.0079780460	0.4003004788
H77	-4.4067179747	0.9891556884	0.0444977211
C78	-4.4656403691	-0.9997955765	2.8411297247
C79	-4.4849715649	-0.9895904744	4.2481797070
H80	-3.5649857758	-0.7767431022	4.7847517288
C81	-5.6709280059	-1.2402526938	4.9317452725
H82	-5.6741011075	-1.2262212582	6.0191425861
C83	-6.8490916988	-1.5086640692	4.2326342127
H84	-7.7721834314	-1.7052520677	4.7719189874
C85	-6.8335154522	-1.5250623723	2.8365242301
H86	-7.7454604736	-1.7386119635	2.2841042195
C87	-5.6550323808	-1.2744380750	2.1399791165
H88	-5.6325031731	-1.2960176711	1.0540967970
Ta89	-1.2792696352	0.9206652122	-1.5736753355
Ta90	-0.2060455097	-1.9833567331	-0.9806115666
Ta91	1.8088255836	0.4273567693	-1.2170053725
N92	0.2040941221	-0.3947175746	-2.4764755010
N93	-2.1754757491	-0.9094017597	-0.9059241824
N94	-2.2907007824	1.7218594681	-2.8117794926
N95	-0.4349557612	-3.5725637237	-1.7644629300
N96	-0.5451980369	-2.1728011567	1.1670576029
N97	1.8508676926	-1.6652733032	-0.4382430588
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C102	-0.6861467758	-1.0856675521	-6.0489282211

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C106	1.6216129163	-1.6626984342	-5.6962225772
H107	2.5705871049	-2.0455939134	-6.0638198440
C108	1.5163698765	-1.2737750666	-4.3625989213
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C110	-3.3839518773	-1.5489229644	-1.3310008455
C111	-4.3019630879	-0.9132659800	-2.1815829369
H112	-4.0988800787	0.0929828892	-2.5309936314
C113	-5.4657948124	-1.5674003389	-2.5856698607
H114	-6.1593325682	-1.0528327128	-3.2466535929
C115	-5.7402394683	-2.8654008537	-2.1567583228
H116	-6.6460959722	-3.3727311947	-2.4778794453
C117	-4.8338990441	-3.5045216495	-1.3094739761
H118	-5.0262588954	-4.5170890200	-0.9635752055
C119	-3.6726100149	-2.8559801355	-0.8989428824
H120	-2.9783068384	-3.3690053734	-0.2399955124
C121	-3.0569554648	2.3803015742	-3.7516277150
C122	-4.2951920193	2.9444952228	-3.3910477652
H123	-4.6282923767	2.8686315786	-2.3596113537
C124	-5.0700778343	3.5951596980	-4.3472031878
H125	-6.0246605740	4.0275181075	-4.0564825047
C126	-4.6311908977	3.6947605645	-5.6685268003
H127	-5.2411757176	4.2031751518	-6.4107669471
C128	-3.4021638230	3.1391745765	-6.0298891889
H129	-3.0510158658	3.2145534868	-7.0562429247
C130	-2.6168210874	2.4863278021	-5.0845978931
H131	-1.6605423803	2.0499206476	-5.3578098065
C132	-0.6491723913	-4.7863049571	-2.3834555104
C133	-0.7431947644	-5.9651546566	-1.6200170167
H134	-0.6490699902	-5.9004242857	-0.5391929943
C135	-0.9506041688	-7.1895060768	-2.2496777296
H136	-1.0231660679	-8.0935833490	-1.6494258518
C137	-1.0663872218	-7.2599938203	-3.6386096808
H138	-1.2261181260	-8.2185013233	-4.1258951549
C139	-0.9751014252	-6.0918252296	-4.3989783779
H140	-1.0652012493	-6.1393660934	-5.4815205488
C141	-0.7690390183	-4.8609336310	-3.7837549305
H142	-0.6948227073	-3.9473484965	-4.3672507794
C143	-0.7186345497	-3.4399131000	1.8123031319
C144	-1.9254936414	-3.7924316562	2.4346555162
H145	-2.7548577550	-3.0947597270	2.4250511781
C146	-2.0609881124	-5.0244860718	3.0733444452
H147	-3.0063202604	-5.2710094035	3.5507718031

C148	-1.0008456398	-5.9289233304	3.1103043883
H149	-1.1087808696	-6.8852122459	3.6151072141
C150	0.2034768238	-5.5872032378	2.4929222996
H151	1.0449730680	-6.2754811199	2.5129490319
C152	0.3439107105	-4.3607841811	1.8482428344
H153	1.2889628253	-4.1095520007	1.3749971050
C154	2.9902567402	-2.5058245121	-0.6455141426
C155	2.8627514971	-3.8296224671	-1.0935170180
H156	1.8764007026	-4.2320602240	-1.2961121547
C157	3.9926545593	-4.6198649153	-1.3019284241
H158	3.8652547684	-5.6405359319	-1.6546581610
C159	5.2709152896	-4.1135557050	-1.0709336278
H160	6.1481109650	-4.7317385106	-1.2421074862
C161	5.4077939045	-2.8006042713	-0.6171758900
H162	6.3950464000	-2.3835907340	-0.4330563041
C163	4.2835951241	-2.0079780460	-0.4003004788
H164	4.4067179747	-0.9891556884	-0.0444977211
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C166	4.4849715649	0.9895904744	-4.2481797070
H167	3.5649857758	0.7767431022	-4.7847517288
C168	5.6709280059	1.2402526938	-4.9317452725
H169	5.6741011075	1.2262212582	-6.0191425861
C170	6.8490916988	1.5086640692	-4.2326342127
H171	7.7721834314	1.7052520677	-4.7719189874
C172	6.8335154522	1.5250623723	-2.8365242301
H173	7.7454604736	1.7386119635	-2.2841042195
C174	5.6550323808	1.2744380750	-2.1399791165
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IV. Electrospray Mass Spectra for 3 and 4, Including ^{17}O-, ^{18}O-Enriched Samples

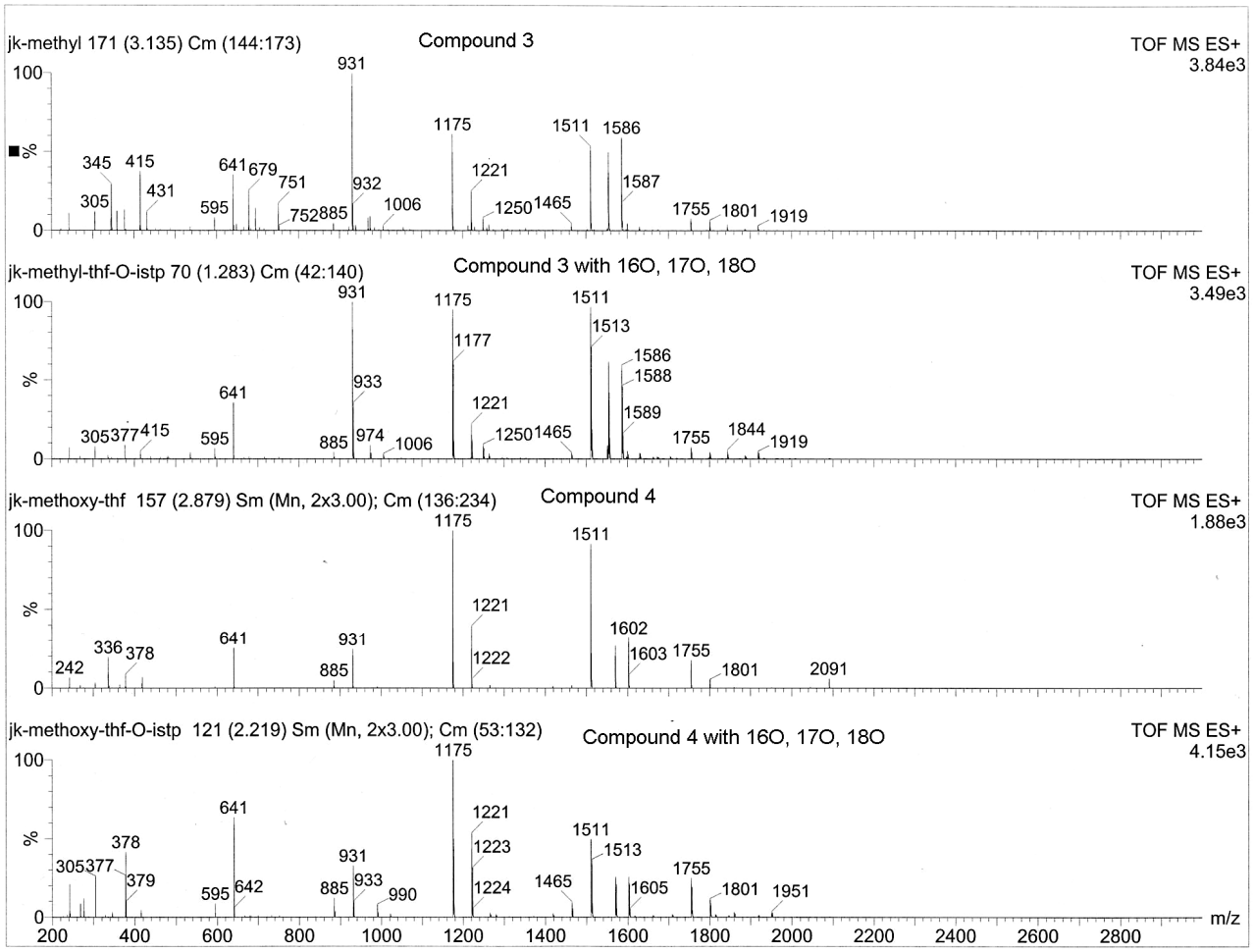

Figure S1. Full spectral width.

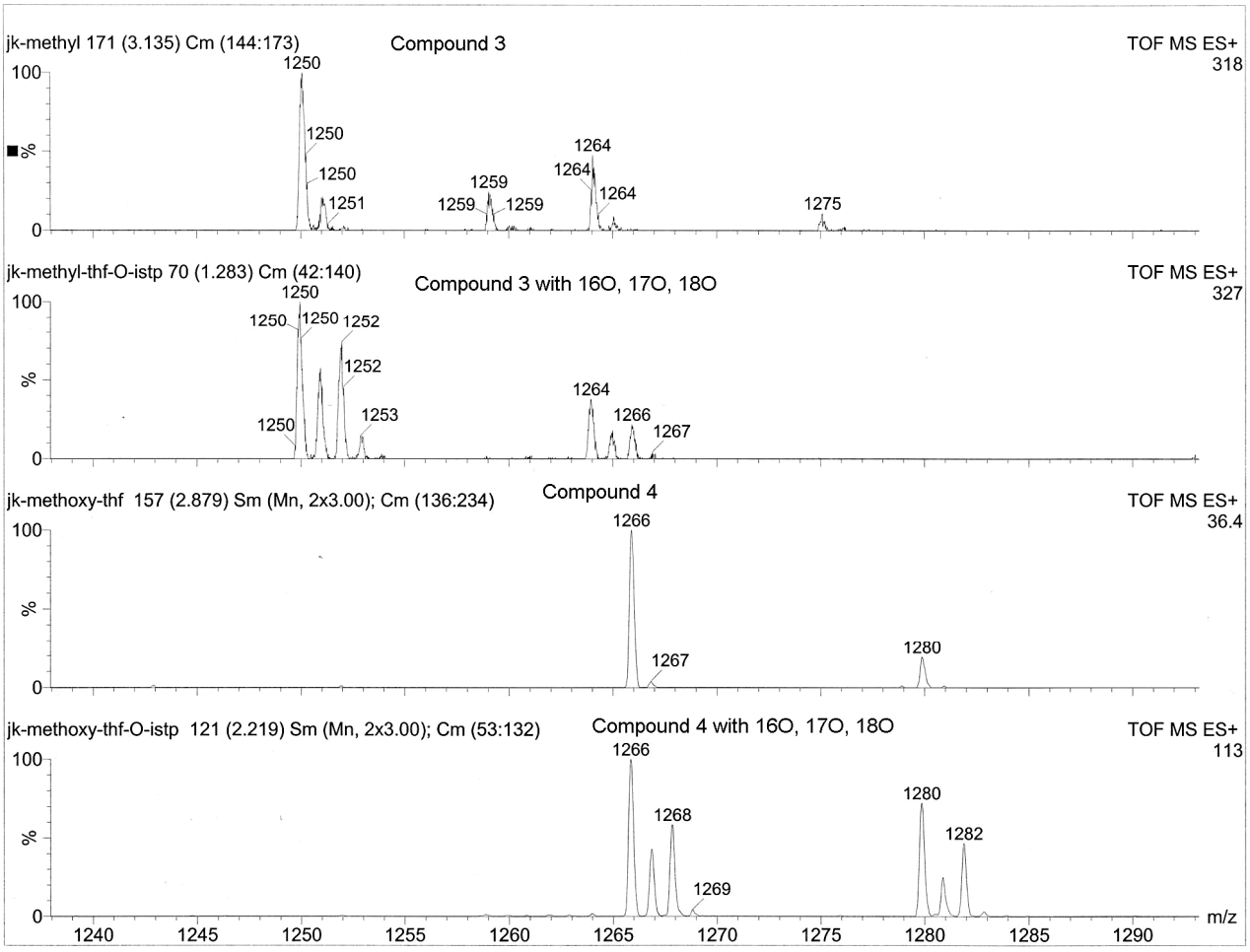

Figure S2. Enlargement #1, showing 16 Da shifts of compound **4** peaks relative to those of **3**.

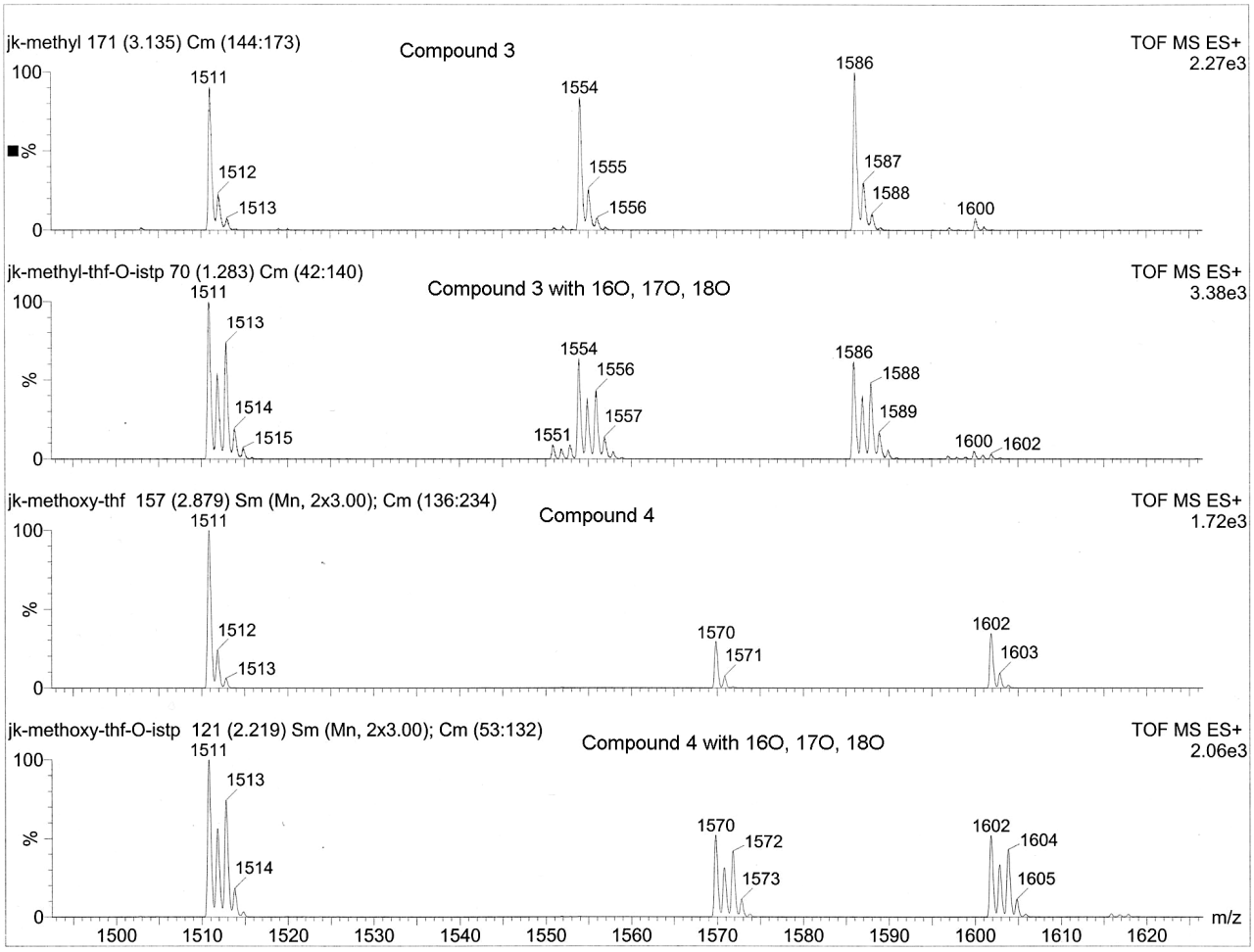

Figure S3. Enlargement #2, showing peak that is common to **3** and **4**, no ligands remaining on cluster core.

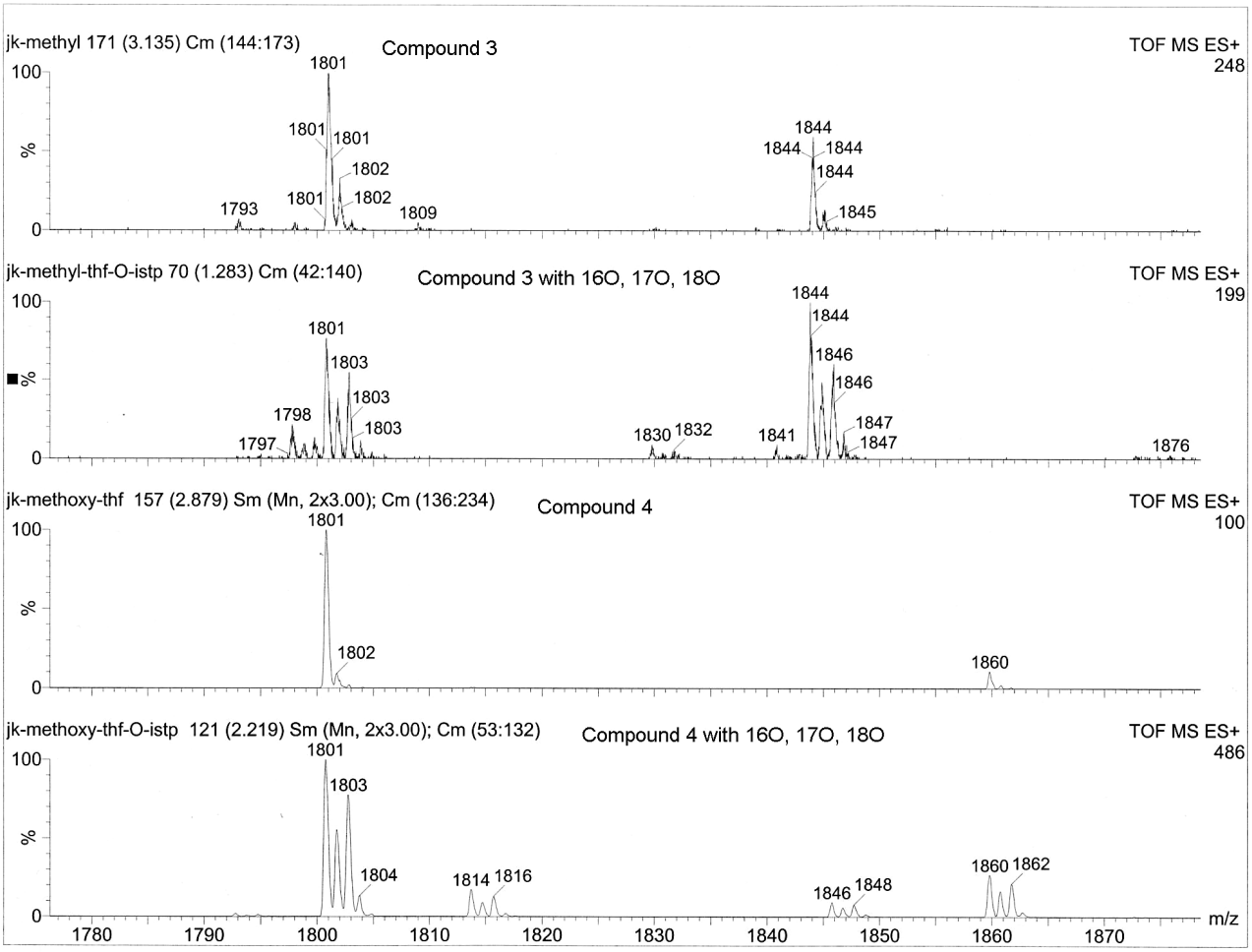

Figure S4. Enlargement #3, showing higher-mass peaks.

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