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Monochloride complex of five-mercury anticrown $[(CF_3)_2CHg]_5$ and reinvestigation of crystal structure of this anticrown

Kirill I. Tugashov, Irina A. Tikhonova, Vladimir B. Shur, Andrei Yu. Volkonsky and Fedor M. Dolgushin

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Table S1. Crystal data and structure refinement parameters for the complexes **5** and **6**.

Crystal data	**5**	**6**
Chemical formula	$C_{15}F_{30}Hg_5 \cdot 2(Cl) \cdot 2(C_5H_6N)$	$C_{15}F_{30}Hg_5 \cdot Cl \cdot C_5H_6N$
M_r	1984.22	1868.66
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, P-1
Temperature (K)	210	110
a, b, c (Å)	16.549 (3), 14.025 (3), 18.106 (4)	12.8129 (16), 13.1823 (17), 21.548 (3)
β (°)	91.105 (5)	78.002 (3), 81.070 (3), 75.252 (3)
V (Å^3)	4201.5 (15)	3422.5 (8)
Z	4	4
F(000)	3520	3280
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	18.49	22.61
Crystal size (mm)	0.34 × 0.28 × 0.22	0.30 × 0.10 × 0.10
Data collection		
Diffractometer	Bruker *SMART* 1000 CCD	Bruker *SMART* 1000 CCD
Absorption correction	Multi-scan *SADABS* 2016/2[S1]	Multi-scan *SADABS* 2016/2
T_{min}, T_{max}	0.003, 0.022	0.072, 0.211
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44263, 11166, 8157	36173, 16502, 10454
R_{int}	0.064	0.059
θ values (°)	θ_{max} = 29.0, θ_{min} = 1.8	θ_{max} = 28.0, θ_{min} = 1.0
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.111, 0.83	0.051, 0.116, 1.06
No. of reflections	11166	16502
No. of parameters	572	959
No. of restraints		25
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.81, –2.09	5.07, –3.55

Experimental Section

Materials and methods. Because of the suspected toxicity of the mercury compounds studied in this work, great care should be exercised during their synthesis, handling and storage. Commercial $(PhCOO)_2Pb{\cdot}H_2O$ (Hölzel-Biotech) was used without additional purification. Solvents were purified by conventional methods and freshly distilled prior to use over CaH_2 (ethanol and pyridine) and $LiAlH_4$ (diethyl ether) under Ar. The ^{19}F NMR spectra were measured on a Bruker Av-300 instrument using $CFCl_3$ as external standard.

Synthesis of $(PyH)_2\{[(CF_3)_2CHg]_5\}Cl_2$ (5). The starting complex **5** was prepared according to the published procedure[S2] (where it was erroneously described as $[(CF_3)_2CHg]_5{\cdot}2Py{\cdot}2H_2O$), re crystallised from ethanol and dried in vacuum at 20°C for 3 h. Anal. calcd. for $C_{25}H_{12}N_2F_{30}Cl_2Hg_5$ (%): C, 15.13; H, 0.61; F, 28.72. Found: C, 15.30; H, 0.65; F, 28.59. ^{19}F NMR (acetone-d_6, δ, ppm): –45.9 (s with satellites, $^3J_{FHg}$ = 237 Hz). The obtained data correspond to the literature.

Synthesis of $(PyH)\{[(CF_3)_2CHg]_5\}Cl$ (6). To a suspension of $(PhCOO)_2Pb{\cdot}H_2O$ (0.0235 g, 0.05 mmol) in EtOH (4 mL) was added a solution of **5** (0.0990 g, 0.05 mmol) in EtOH (3 mL). The resulting mixture that quickly became cloudy was vigorously stirred for 30 min at 20°C, then centrifuged for 20 min (4000 RPM), filtered off, and the supernatant was completely evaporated. The obtained solid residue was extracted with diethyl ether (2×3 mL), and this extract was allowed to slowly evaporate to ~0.5 mL overnight. The precipitated colourless crystals of **6** were filtered off, washed with cold CH_2Cl_2 (2 × 0.5 mL) and dried in vacuum at 20°C for 3 h. Yield of **6**: 0.0288 g (31%). Anal. calcd. for $C_{20}H_6NF_{30}ClHg_5$ (%): C, 12.86; H, 0.32; F, 30.50. Found: C, 12.98; H, 0.55; F, 30.21. ^{19}F NMR (acetone-d_6, δ, ppm): –46.1 (s with satellites, $^3J_{FHg}$ = 231 Hz). The crystals of **6** for the X-Ray diffraction study were grown from EtOH solution.

X-ray Diffraction Study. Diffraction data for **5** and **6** were collected on a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation. Semiempirical absorption correction based on equivalent reflections was applied using the SADABS program.[S3] The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[S4,S5] The hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation with $U_{iso}(H) = 1.2U_{eq}(C)$. Molecular graphics were drawn using the SHELX software. For carrying out the X-ray diffraction study, the samples of crystals of **5** and **6** were not washed and dried in vacuum.

MS Study. High-resolution mass spectra were recorded on a LCMS-9030 device (Shimadzu, Japan) by electrospray ionization mass spectrometry (ESI-MS). Measurements were carried out in negative ion mode; samples were dissolved in acetonitrile and injected into the mass-spectrometer chamber from an HPLC system LC-40 Nexera (Shimadzu, Japan). The following parameters were used: capillary voltage 4.0 kV; mass scanning range: m/z 150–4000; external calibration with solution NaI in $MeOH/H_2O$; drying and heating gases (nitrogen) (each

10 L/min); nebulizing gas (nitrogen) (3 L/min); interface temperature: 300°C; flow rate acetonitrile (100%) 0.4 mL/min. Molecular ions in the spectra were analyzed and matched with the appropriately calculated *m*/*z* and isotopic profiles in the LabSolutions v.5.114 program.

References

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S3. *SADABS, Version 2016/5*, Bruker AXS, Madison, WI, 2016.

S4. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112; https://doi.org/10.1107/S0108767307043930.

S5. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3; https://doi.org/10.1107/S2053229614024218.

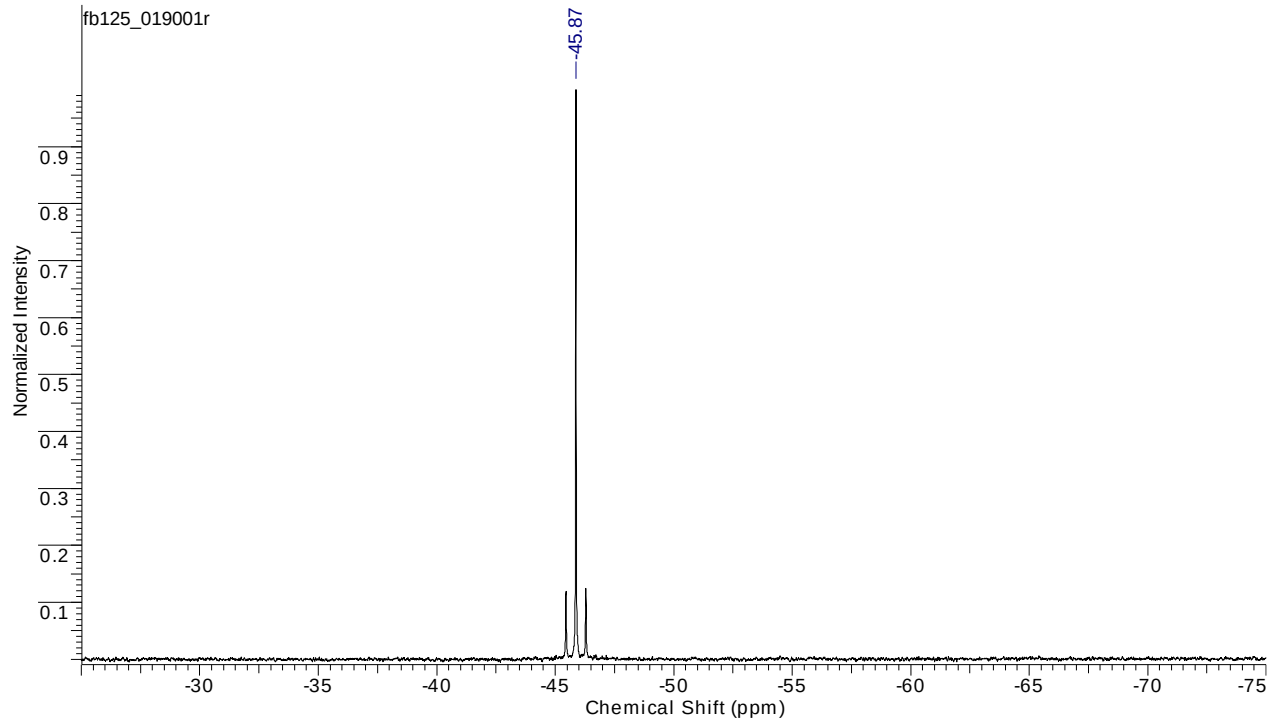

Figure S1. ^{19}F NMR spectrum of complex **5** in acetone-d_6.

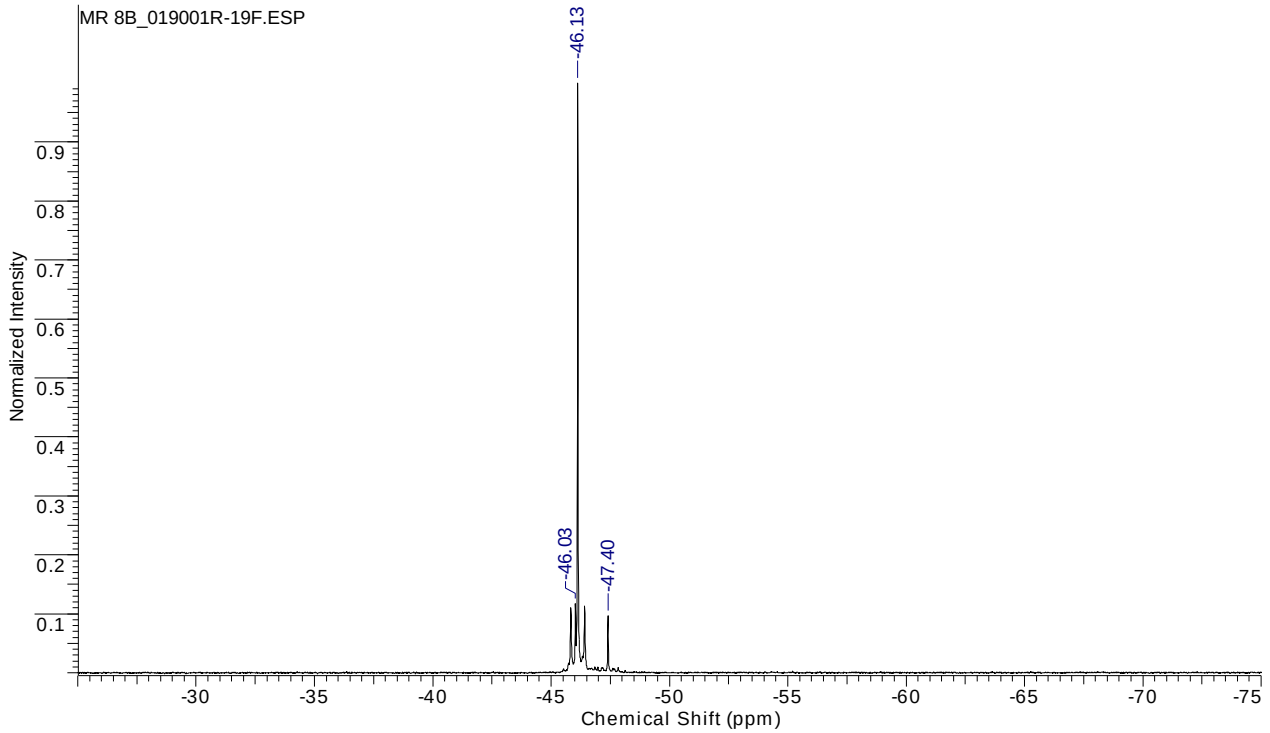

Figure S2. ^{19}F NMR spectrum of complex **6** in acetone-d_6.

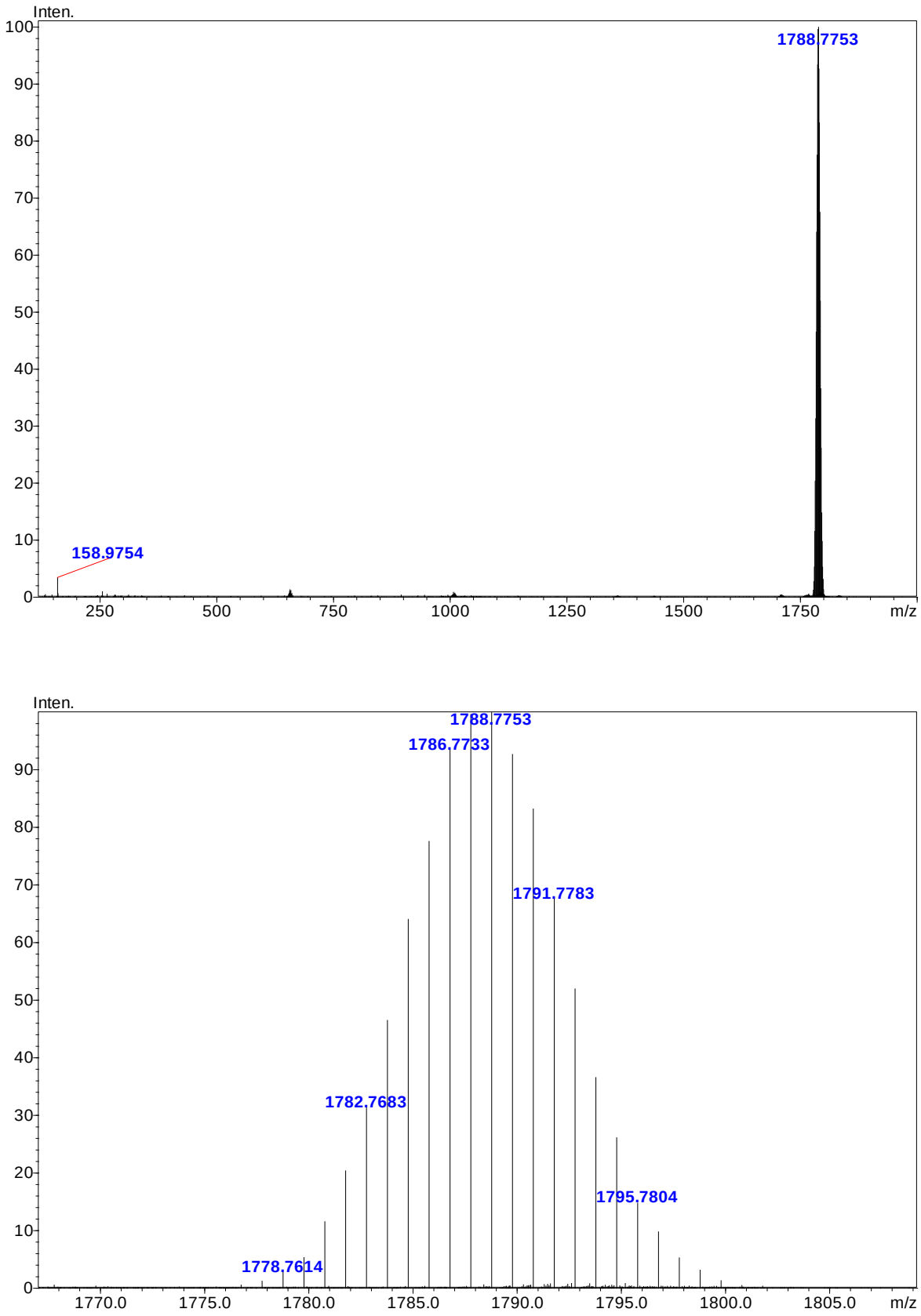

Figure S3. ESI-MS spectrum of complex **5** in acetonitrile.

The maxima molecular ion peaks at –1787.7742 (int. 99%) and –1788.7753 (int. 100%) correspond to $\{[(CF_3)_2C^{202}Hg]_2[(CF_3)_2C^{200}Hg]_2[(CF_3)_2C^{199}Hg]\}^{35}Cl^-$ and $\{[(CF_3)_2C^{202}Hg]_2[(CF_3)_2C^{200}Hg]_3\}^{35}Cl^-$, respectively.

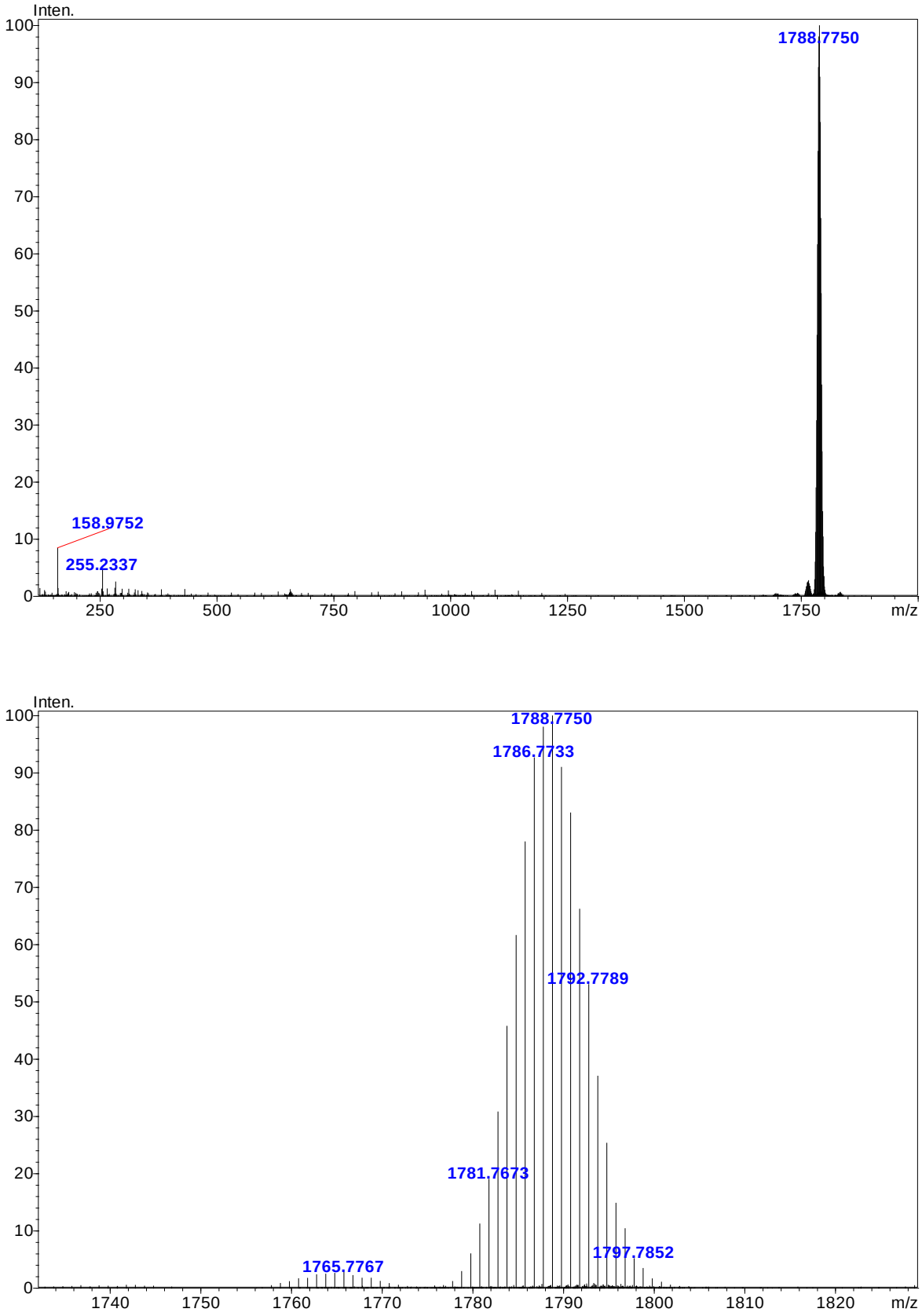

Figure S4. ESI-MS spectrum of complex **6** in acetonitrile.

The maxima molecular ion peaks at –1787.7741 (int. 98%) and –1788.7750 (int. 100%) correspond to $\{[(CF_3)_2C^{202}Hg]_2[(CF_3)_2C^{200}Hg]_2[(CF_3)_2C^{199}Hg]\}^{35}Cl^-$ and $\{[(CF_3)_2C^{202}Hg]_2[(CF_3)_2C^{200}Hg]_3\}^{35}Cl^-$, respectively.