

A Synthetic Model of Hg(II) Sequestration

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Supplementary Information (ESI)

Experimental

Methods and Materials

Starting materials were of commercially available reagent quality. Elemental analyses were carried out by Atlantic Microlab, Inc., Norcross Georgia.

NMR Spectroscopy

¹H and ¹³C NMR spectra were recorded in 5-mm-o.d. NMR tubes on a Varian Mercury 400VX operating in the pulse Fourier transform mode. The sample temperature was maintained by blowing chilled air over the NMR tube in the probe. Chemical shifts were measured relative to internal solvent but are reported relative to tetramethylsilane. Coupling constants are ³J(¹H¹H) reported in Hz.

Mass Spectrometry

ESI-MS spectra were obtained on a LCQ-DECA ion trap mass spectrometer (Thermo) equipped with an ESI source. Dilute solutions (nominally 5 x 10⁻⁴ M) of the Hg/ligand complexes in acetonitrile were directly infused into the ESI source at flow rates in the range of 5-15 μL/min. Ion focusing conditions were optimized to maximize ion signal, while maintaining as low a capillary voltage as possible in order to minimize dissociation of metal-ligand complexes upon ionization and transfer to the ion trap. Similar ionization conditions routinely produce intact non-covalent cluster ions in our instrument. MS/MS spectra were obtained by isolating the parent ion at q_z = 0.250, with isolation widths adjusted to isolate the entire Hg isotopic distribution. Parent ions are allowed to undergo collision-induced dissociation with the background helium buffer gas at various activation amplitudes in the range of 10-30% (normalized collision energy).

X-ray Crystallography

Complete crystallographic data are given in the CIF files. All data were collected at 20 °C using graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å). Data for **2** were collected on a Siemens R3 four-circle diffractometer using the θ - 2θ technique over a 2θ range of 3 - 55°. The structure was solved by direct methods and Fourier difference maps using the SHELXS-86 [10] package of software programs. Final refinements of both structures were done using SHELXL-97 [9] minimizing R2 = [Σ[w(F_o²) - (F_c²)²]/Σ[w(F_o²)²]^{1/2}, R1 = Σ||F_o| - |F_c||/Σ |F_o|, and S = [Σ[w(F_o² - F_c²)²]/(n - p)]^{1/2}. All non-hydrogen atoms were refined as anisotropic, the hydrogen atomic positions were fixed relative to the bonded carbons, and the isotropic thermal parameters were refined.

X-ray Powder Diffraction

Powder diffraction analysis was carried out on a Bruker *SMART Apex II* diffractometer using graphite-monochromated Cu K α radiation.¹ Samples were ground and prepared as mulls using Paratone N oil. Four 180 s frames were collected, covering 8–100° 2 θ . Frames were merged using the *SMART Apex II* software¹ and were further processed using *DIFFRAC-Plus* and *EVA* software.²

Synthesis of Hg(L)(ClO₄) (1): A solution of Hg(ClO₄)₂•3H₂O (1.36 g, 3.00 mmol) in methanol (30 mL) was added slowly with stirring to a solution of LH³ (0.505 g, 3.00 mmol) and triethylamine (422 μ L, 3.00 mmol) in methanol. A fine white precipitate formed. The white powder (1.35 g, 2.89 mmol, 96 % yield) was isolated by filtration and dried under vacuum. Mp: dec. 138 °C (from MeOH). ¹H NMR δ_{H} [300 MHz, 5 mM CD₃CN, 338 K] 8.58 (d, 1H, J = 5 Hz, H_a), 8.03 (1H, t, J = 8 Hz, H_c) 7.60 (1H, dd, J = 5,8 Hz, H_b) 7.55 (1H, d, J = 8 Hz, H_d), 4.33 (3H, bs, H_e, H_f), 3.24 (2H, bs, H_g, H_h). Elemental Analysis (%), calc. for C₈H₁₁N₂O₄ClSHg, C 20.56, H 2.37, N 5.99, found, C 20.82, H 2.33, N 6.00.

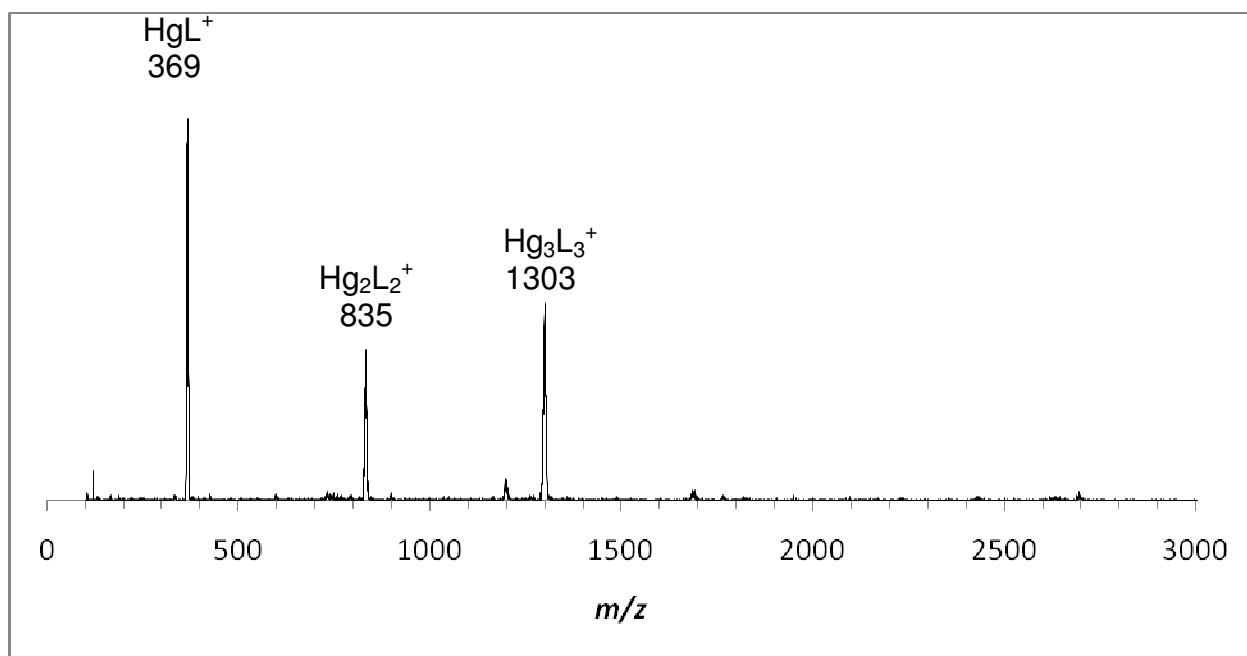


Figure S1. ESI-MS spectrum for nominally 0.5 mM acetonitrile solution of HgLCIO₄ precipitate (1).

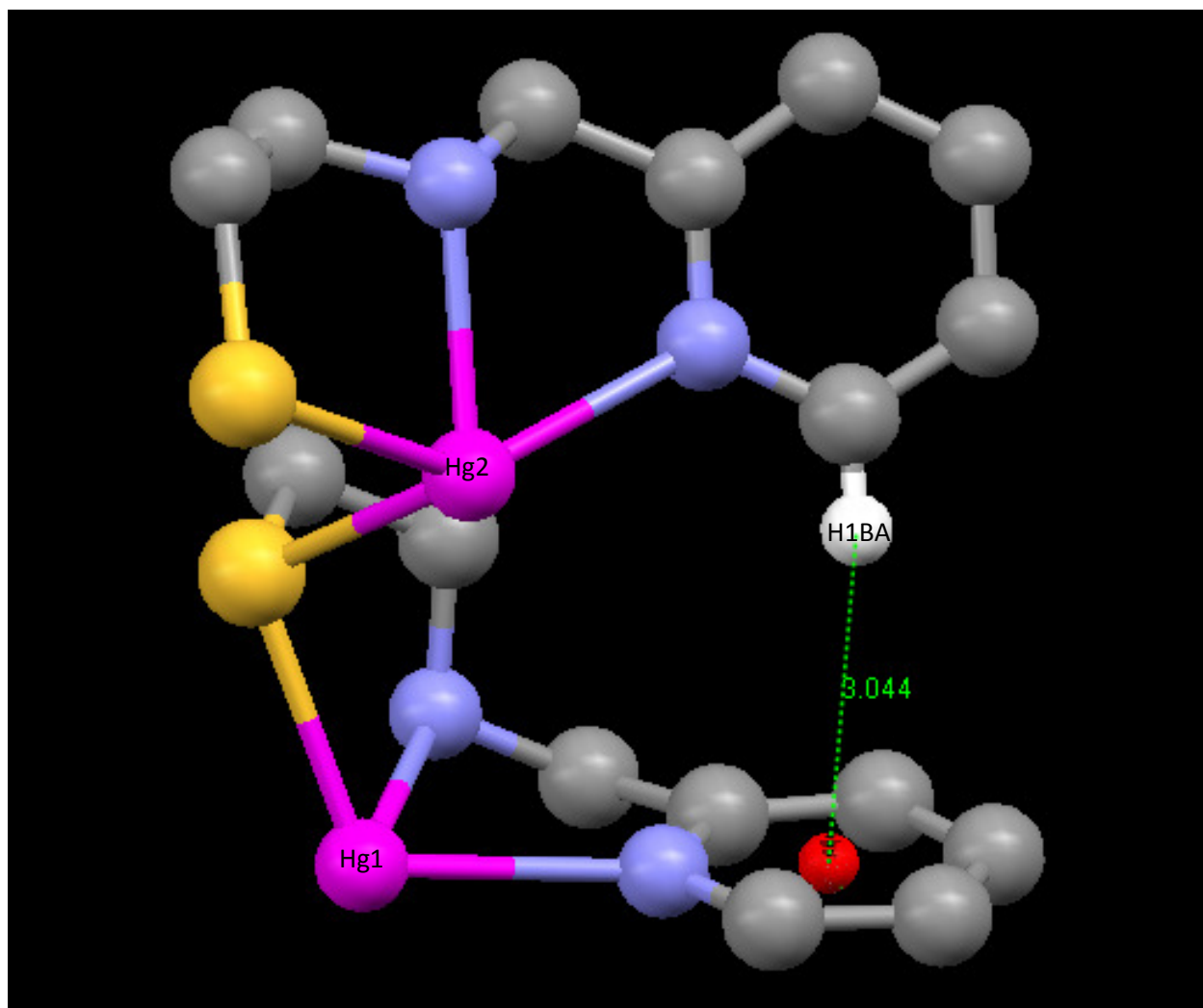


Figure S2. Highlight of the structure of **2** showing the relative orientation of the pyridyl ring bound to Hg2 and one of the pyridyl rings bound to Hg1. Note H1BA is located 3.044 Å above the centroid of the neighboring pyridyl, a position subject to strong ring current exposure.

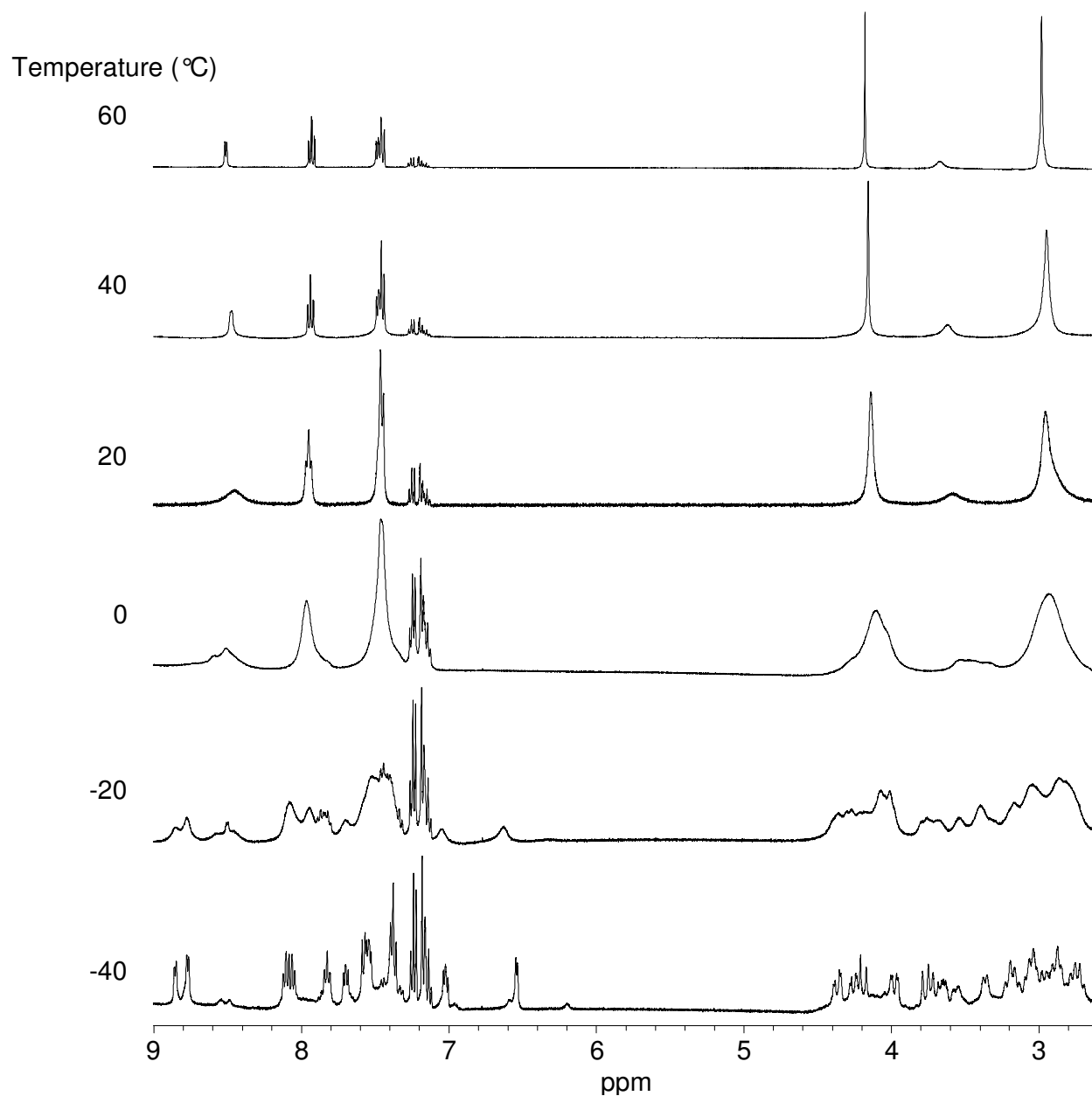


Figure S3. Proton NMR spectrum of a nominally 1 mM solution of [Hg₅L₆](ClO₄)₄·toluene in CD₃CN as a function of temperature. At 60 °C, a single exchange averaged ligand environment is observed. At -40 °C, there are three major ligand environments in slow exchange on the chemical shift time scale. Spectra were qualitatively similar in acetone-*d*₆. Conditions for slow exchange on the $J(^{199}\text{Hg}^1\text{H})$ time scale were not found over the accessible temperature range for dilute solution of **2** in either CD₃CN or acetone-*d*₆.

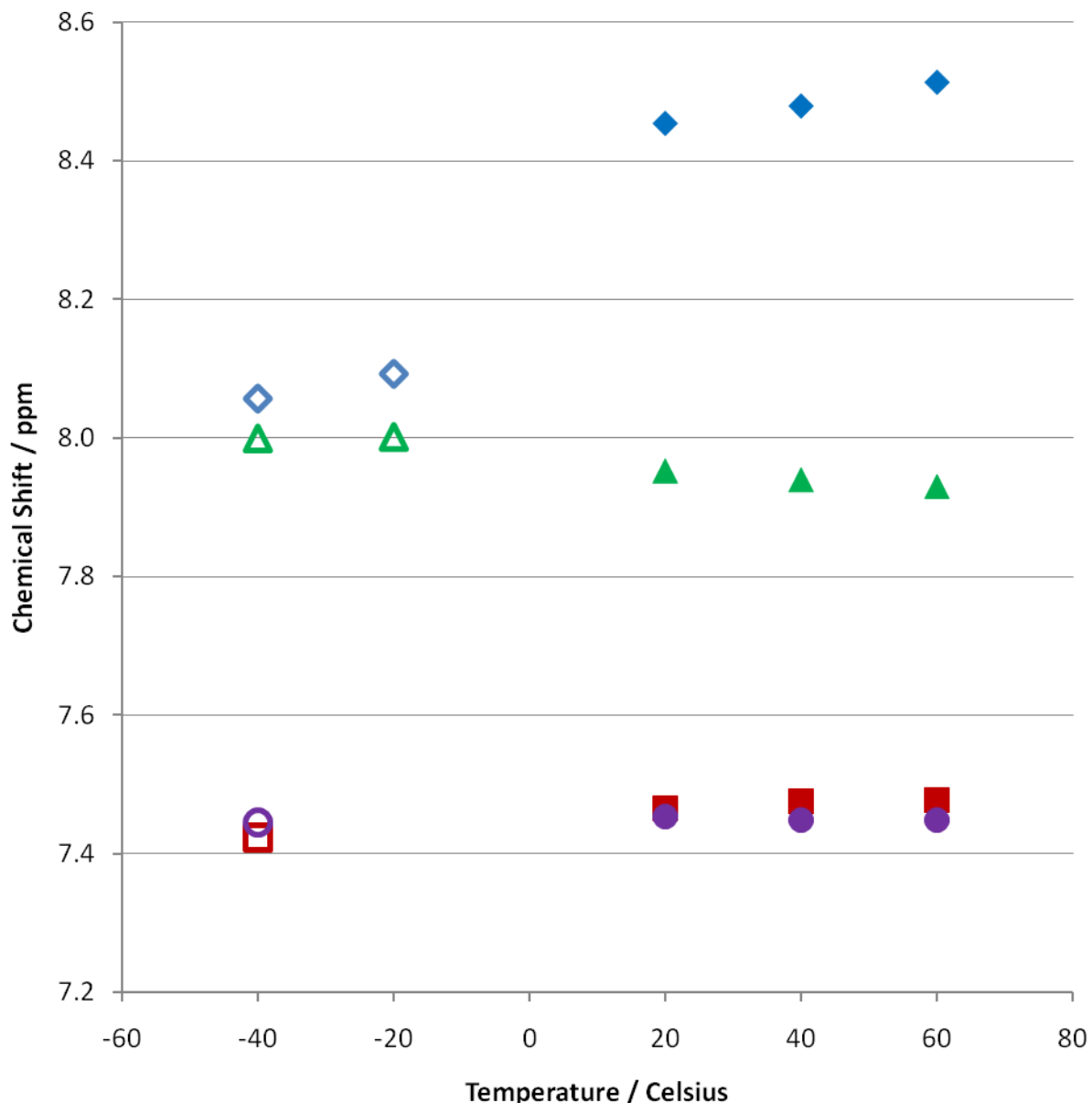


Fig. S4. Trends in ^1H chemical shifts for pyridyl protons of **L** as a function of temperature for 1 mM $[\text{Hg}_5\text{L}_6](\text{ClO}_4)_4$ (**2**) in CD_3CN . The exchange averaged chemical shifts observed at 20 °C and above are indicated by solid markers. Open markers correspond to mole fraction weighted averages of the three most prevalent chemical shift environments observed at cryogenic temperatures assuming a 1:1:1 ratio (at -20 °C, H_c and H_d were not adequately resolved for assignment). \diamond , \blacklozenge H_a ; \square , \blacksquare H_b ; \triangle , \blacktriangle H_c ; \circ , \bullet H_d . Data acquired at elevated temperature are consistent with rapid exchange between a variety of closely related ligand environments. The average chemical shifts for H_a in the three most prevalent ligand environments below -20 °C are far from the values expected if these environments were the only environments in rapid exchange at elevated temperature. The proportional loss of the three ligand environments upon titration with $\text{Hg}(\text{ClO}_4)_2$ and the strong upfield shift of one H_a observed below -20 °C are consistent with the crystallographic structure of the cation of **2**.

Supplementary Information References:

1. *SMART Apex II, Data Collection Software*, version 2.1; Bruker AXS Inc.: Madison, WI, 2005.
2. *DIFFRAC Plus*, version 10.0 and *EVA*, release 2004; Bruker AXS Inc.: Madison, WI, 2005.
3. Brand, U., Vahrenkamp, H. *Inorg. Chem.* **1995**, *34*, 3285.