Supplementary Information

Intramolecular Hg−−π interactions of d-character with non-bridging atoms in mercury-aryl complexes

Anthony Lannes, Alain Manceau, Mauro Rovezzi, Pieter Glatzel, Yves Joly, and Isabelle Gautier-Luneau

Materials and methods

Synthesis. Thiophene (99 %) and 2,2’-bithiophene (98 %) were purchased from Alfa Aesar and mercury acetate (98 %) was purchased from Merck. Methanol was purchased from Roth and was of analytical grade. All reagents and solvent were used without further purification. All reactions were carried out in aerobic conditions.

[Hg₂(AcO)₂(BTph)] (1): 116 mg (0.7 mmol) of 2,2'-bithiophene were solubilized in 2 mL MeOH under stirring. To this clear colorless solution were added 445.5 mg (1.4 mmol) [Hg(AcO)] in 10 mL MeOH. A white precipitate appeared in the colorless solution after one hour stirring. 400 mg were collected in a filter for characterization by powder X-ray diffraction (yield of 88 %, based on Hg) and IR (Nicolet ATR): 3066 (w), 2985 (w), 2931 (w), 1593 (s), 1489 (w), 1427 (w), 1408 (w), 1365 (s), 1300 (s), 1196 (w), 1049 (m), 1022 (m), 964 (m), 929 (m), 872 (m), 798 (s), 763 (w), 741 (w), 690 (s) cm⁻¹. Crystals were obtained by slow diffusion in a test tube: 41.5 mg (0.25 mmol) of 2,2'-bithiophene were solubilized in 1 mL MeOH, then 15 mL MeOH were meticulously deposited on this solution, and upon it were deposited 158 mg [Hg(AcO)] (0.5 mmol) in 3 mL MeOH. Plate-like crystals appeared after 3 days.

[Hg₂(AcO)₂(Tph)] (2): Its synthesis differs from 1 by the use of thiophene (60 mg, 57 µL 0.7 mmol) instead of 2,2’-bithiophene. Yield of the powder: 95 %, based on Hg. IR (Nicolet ATR): 1581 (s), 1489 (w), 1458 (w), 1427 (w), 1365 (m), 1308 (s), 1203 (w), 1157 (w), 1111 (w), 1022 (m), 972 (w), 926 (m), 841 (m), 791 (m), 763 (m), 741 (w), 694 (s) cm⁻¹. Plate-like crystals were obtained in the same manner as for 1 after three days with 21 mg thiophene (20 µL, 0.25 mmol) instead of 2,2’-bithiophene.

Crystal structure determination. Single crystals were mounted at 293 K on a Bruker KappaCCD diffractometer with monochromatic AgKα radiation (λ = 0.56087 Å). The crystal structures were solved using SIR 92¹ as implemented in CRYSTALS²,³ through the WinGX program suite. The refinements were performed with anisotropic thermal parameters for all non-H atoms. H atoms were generated at idealized positions, riding on the carrier atoms, with isotropic thermal parameters.

Crystal Data for 1: C₁₂H₁₀Hg₂O₄S₂, M = 683.50 g mol⁻¹, crystal dimension 0.072 x 0.379 x 0.388 mm³, monoclinic, space group P2₁/a (N°14), a = 8.1729(1) Å, b = 5.2175(1) Å, c = 17.3973(1) Å, β = 99.70(3)°, V = 731.24(2) Å³, Z = 2, ρ calc = 3.104 g cm⁻³, μ = 11.625 mm⁻¹, 2θ max = 21.42°, electronic residual -3.85/2.96 e Å⁻³, 9384 measured reflections collected (R int = 0.078), 91 refined
parameters for 1127 unique reflections. Final $R$ indices ($I > 3\sigma$): $R(F) = 0.0796$, $\omega R(F^2) = 0.0921$. CIF file can be obtained free of charge in the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC-1438075.

Crystal Data for $2$ : $C_8H_8Hg_2O_4S$, $M = 601.40$ g.mol$^{-1}$, dimension $0.034 \times 0.113 \times 0.115$ mm$^3$, monoclinic, space group $P2_1/m$ (N°11), $a = 5.1039(1)$ Å, $b = 16.8784(1)$ Å, $c = 6.6915(1)$ Å, $\beta = 105.28(1)^\circ$, $V = 556.07(2)$ Å$^3$, $Z = 2$, $\rho_{calc} = 3.592$ g.cm$^{-3}$, $\mu = 15.180$ mm$^{-1}$, $2\theta_{max} = 21.41^\circ$, electronic residual $-4.75/4.18$ e/Å$^3$. 6526 measured reflections collected ($R_{int} = 0.0910$), 70 refined parameters for 931 unique reflections. Final $R$ indices ($I > 3\sigma$): $R(F) = 0.0778$, $\omega R(F^2) = 0.0854$. CIF file can be obtained free of charge in the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC-1438076.

**Powder X-Ray Diffraction.** Powder patterns were collected under ambient conditions with a Siemens D5000 diffractometer and copper radiation ($\lambda CuK\alpha_1 = 1.54056$ Å, 40 mA, 40 kV) in the 2$\theta$ scan range 7–70$^\circ$ for $1$ and 6–70$^\circ$ for $2$ with a step size of 0.032$^\circ$ and an acquisition time of 28 s/step. The overlay plots of the powder patterns for $1$ and $2$ with their respective calculated diagrams from the crystal structures show that the two synthetic phases are pure (Fig. S1).

**XANES spectroscopy.** $1$ and $2$ were finely ground, mixed with boron nitride to a concentration of approximately 100 mg/kg (ppm) to prevent overabsorption and prepared as pressed pellets. Each pellet was mounted in a poly(ether ether ketone) (PEEK) sample holder with 2.5 mm path length and sealed with Kapton tape. The two Hg L$_3$-edge spectra were measured in high energy-resolution fluorescence yield detection mode with analyzer crystals on beamline ID26 at the European Synchrotron Radiation Facility (ESRF). Rejection of higher harmonics and reduction of heat load were achieved with a white beam Pd-coated, flat mirror working under total reflection at 2.5 mrad grazing angle. The incoming beam was monochromated by the 111 reflection of a Si double crystal monochromator, then focused horizontally by a second Pd-coated mirror and vertically by a third Pd-coated mirror. The flux on the sample was approximately $10^{13}$ photon/s in a beam footprint on the sample of $\sim 700$ (H) x 80 (V) µm$^2$ FWHM. The Hg L$_3$ (3d$^{5/2} \rightarrow 2p^{3/2}$) fluorescence line was selected using the 555 reflection of five spherically bent (radius = 0.5 m) Si analyzer crystals (diameter = 100 mm) aligned at 81.8$^\circ$ Bragg angle in a vertical Rowland geometry. The diffracted intensity was measured with a Si drift diode detector in single photon counting mode. The effective energy resolution, obtained by convoluting the total instrument energy bandwidth (spreads of the incident and emitted rays), the SDD resolution ($\sim 160$ eV), and the 3d$^{5/2}$ core-hole width from the L$_{al}$ line was about 3.0 eV, compared to an intrinsic line broadening of about 6.1 eV in conventional fluorescence yield measurement with a solid-state detector. Spectra were collected at a sample temperature of 15 K and a scan time of 15 s to reduce the exposure time, and repeated at different pristine positions on the sample to increase the signal-to-noise ratio. The absence of radiation damage was monitored carefully. The incident energy was scanned from 12260 eV to 12360 eV in 0.2 eV steps. The high energy-resolution XANES spectra were normalized to unity at E = 12360 eV.
Supplementary Figures

Figure S1. X-ray powder patterns for 1 (top) and 2 (bottom) compared to the calculated patterns from the crystal structure.
Figure S2. a) Stacking of 2 along the a axis. The molecular entities are linked together by Hg---O weak contacts at 2.77-2.83 Å from the acetate ligands, leading to ribbons along the a axis. The ribbons are stacked in staggered rows and bridged together by longer Hg---O contacts at 3.01-3.04 Å as seen on b). c) Stacking of 1 along the b axis. Ladder-type structure of the ribbons for 2 (d) and 1 (e).

Figure S3. Geometry optimized [Hg(AcO)(Tph)]_2 complex using ORCA\textsuperscript{6} (MP2-RI/def2-TZVP-ecp). Computational scheme were tested previously on the modeling of the structure and stability of monomeric Hg-thiolate complexes\textsuperscript{7,8}. Input files can be found in Ref. \textsuperscript{7}. Black: bond lengths in angstroms. Blue: atomic charges, in units of elementary charge e, calculated by natural population analysis (NPA).\textsuperscript{9} Natural electron configurations:

\begin{verbatim}
Hg [core] 6s(0.90) 5d(9.68) 6p(0.04) 5f(0.08) 6d(0.03) 7p(0.01)
C (1.99Å) [core] 2s(1.17) 2p(3.46) 3s(0.01) 3p(0.05) 3d(0.04) 4f(0.01)
O (2.04Å) [core] 2s(1.73) 2p(4.98) 3s(0.01) 3p(0.04) 3d(0.04)
S (3.25Å) [core] 3s(1.58) 3p(3.81) 4s(0.01) 3d(0.09) 4p(0.02) 4f(0.01)
\end{verbatim}
Figure S4. \((l,m)\)-projected empty DOS in the final state of Hg, C1, C3, S1, and C4 for the Hg-bithiophene complex \((1)\). The \(\pi\)-interactions between Hg and the thiophene ligand are weak, therefore the \(\pi^*\) molecular orbitals do not split, in contrast to \(2\) (Figure 3d).
Figure S5. \((l,m)\)-projected empty DOS in the final state of Hg, O1, O2, O2’, and C2 for the Hg-thiophene complex (2). Note the absence of π-interactions between Hg and the O2, O2’ and C2 atoms.
Figure S6. a) Mercury-toluene ([C₆H₅Me(AlCl₄)₂]) complex extracted from the molecular structure of Hg(C₆H₅Me)[AlCl₄]₂.¹⁰ The Hg-C1 pair is parallel to the z axis, and the Hg-Cl1 pair 20° off the y direction. b) (l,m)-projected empty DOS. Hg is σ-bonded to C1 (sd(Hg)-pz(C1) hybrid) and Cl1 (s(Hg)-px(C11) hybrid), and π-bound to the C2, C3, C4, and C5 atoms of the arene ligand.

References