Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Toxic Heavy Metal - Pb, Cd, Sn - Complexation by the Octadentate Hydroxypyridinonate Ligand Archetype 3,4,3-LI(1,2-HOPO)

Gauthier J-P. Deblonde[1], Trevor D. Lohrey[1,2], Dahlia An[1], Rebecca J. Abergel[1,3]

[1] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

[2] *Department of Chemistry, University of California, Berkeley, CA 94720, USA*

[3] *Department of Nuclear Engineering, University of California, Berkeley, CA 94720, USA*

Supporting Information

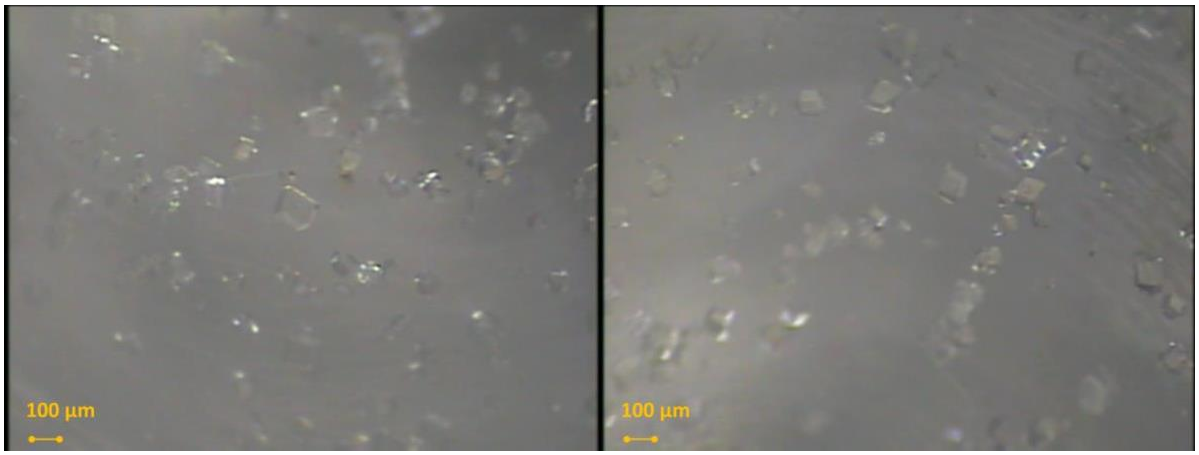

Figure S 1. Single crystal of [Sn^{IV}3,4,3-LI(1,2-HOPO)]·3H2O.

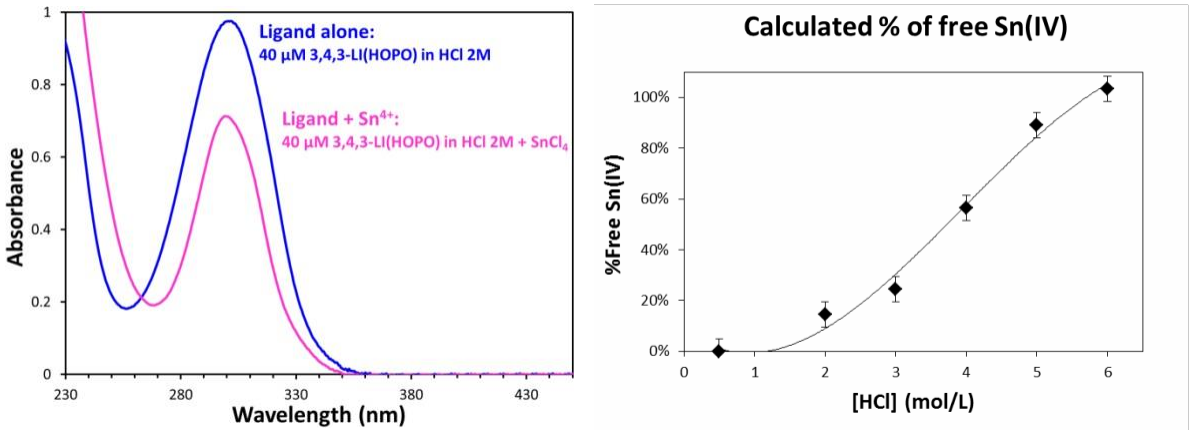

Figure S 2. Left: UV-vis absorbance spectra of samples containing: 40 µM of 3,4,3-LI(1,2-HOPO) and 40 µM of $SnCl_4$ (pink curve) or 40 µM of 3,4,3-LI(1,2-HOPO) (blue curve). Path length: 10 mm. Background electrolyte: HCl 2 M. Absorbance corrected from blank absorbance (HCl 2 M). T = 25 °C. **Right:** Fraction of Sn(IV) released from 3,4,3-LI(1,2-HOPO) as a function of the HCl concentration. The fraction of unbound Sn(IV) was calculated based on the UV-vis absorbance measured at different HCl concentrations.

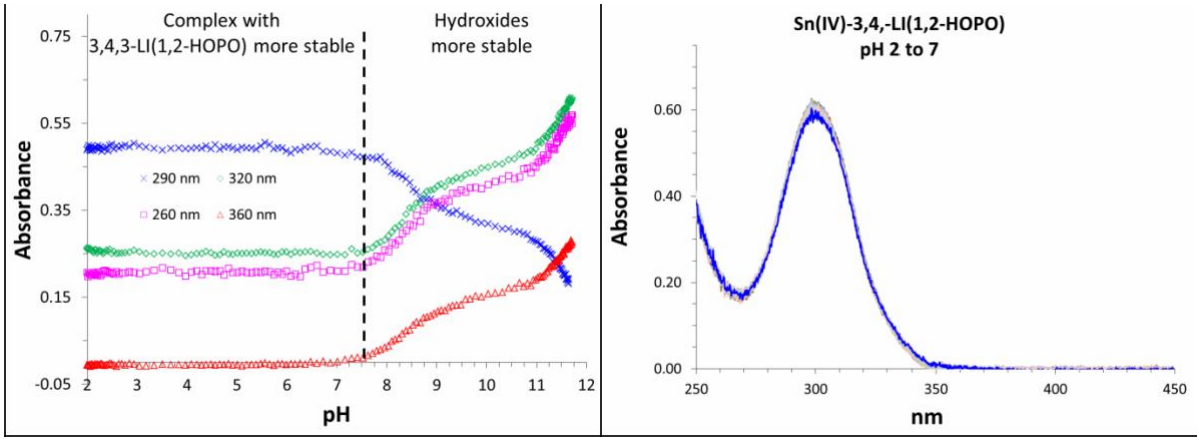

Figure S 3. Absorbance spectra of a solution containing 40 µM of $SnCl_4$ and 40 µM of 3,4,3-LI(1,2-HOPO) as a function of pH. 140 spectra measured between pH 1.5 and 11.7. I = 0.1 M (KCl), T = 25 °C. Path length = 10 mm. **(Left)** Absorbance of the [Sn^{IV}3,4,3-LI(1,2-HOPO)]^0 solution at 260 nm (squares), 290 nm (crosses), 320 nm (diamonds), and 360 nm (triangles) as a function of pH. **(B)** Spectra measured between pH 2.0 and 7.1 (70 spectra overlaid).

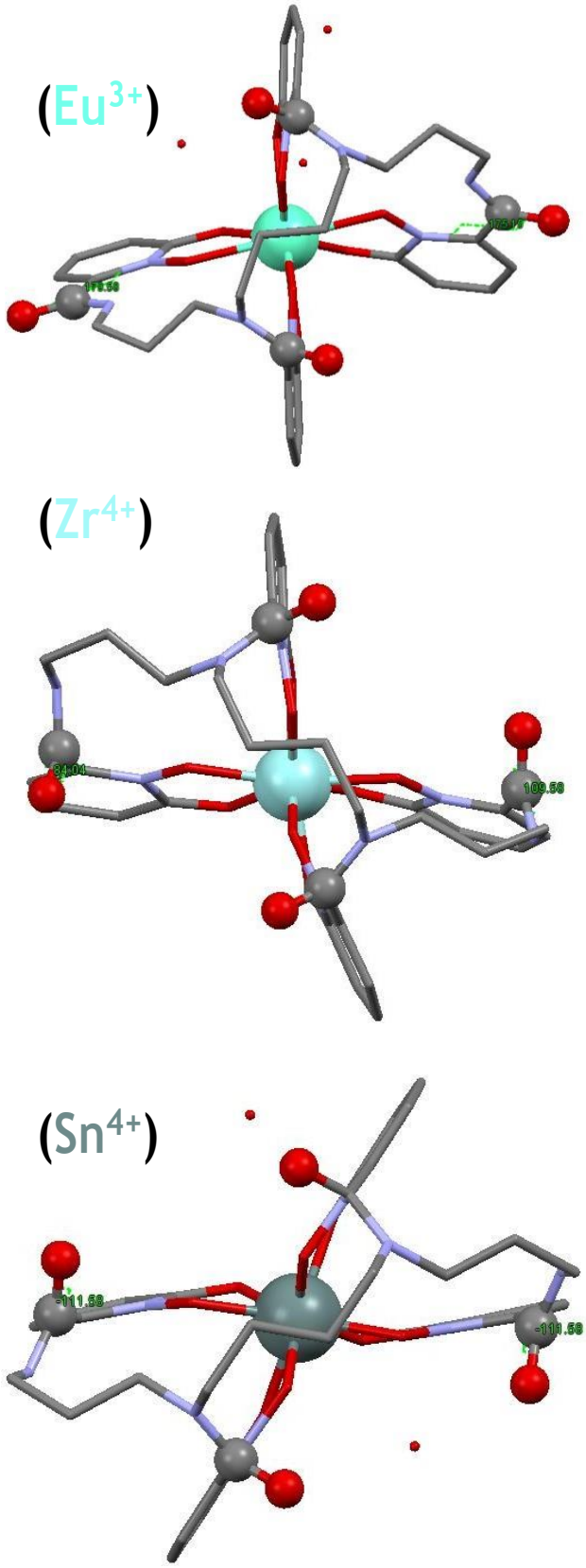

Figure S 4: Top view of the crystal structures of the 3,4,3-LI(1,2-HOPO) complexes with Eu^{3+}, Zr^{4+}, and Sn^{4+}. The metal ions and the C=O amide bonds are displayed as balls and sticks. The rest of the organic ligand is displayed as capped sticks. The torsion angles between the aromatic 1,2-HOPO units and their C=O amide bonds are 179.6° and 175.2° for Eu^{3+}, 84.0° and 109.6° for Zr^{4+} , and 111.6° for Sn^{4+}.

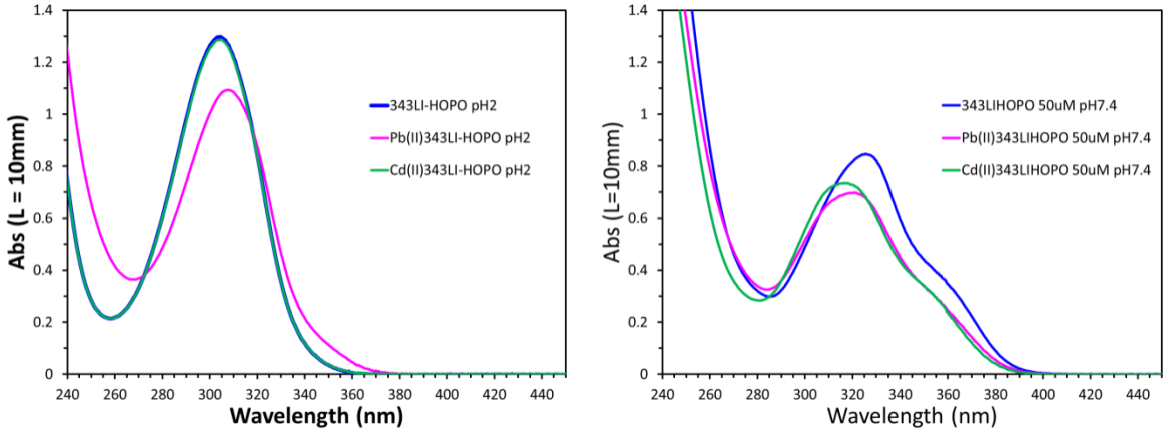

Figure S 5. UV-vis spectra of a 50 μM solution of the ligand 3,4,3-LI(1,2-HOPO) (blue curve), a 50 μM solution of Pb(II)-3,4,3-LI(1,2-HOPO) (pink curve), and 50 μM solution of Cd(II)-3,4,3-LI(1,2-HOPO) (green curve). Right: pH = 7.4. Buffer = 0.1 M HEPES. Left: pH = 2 (HCl). The spectra of the free ligand and the sample containing Cd(II) are superimposed at pH 2 showing the lack of metal binding at this pH.

Table S1. Crystallographic details for $[Sn^{IV}3,4,3\text{-LI}(1,2\text{-HOPO})]\cdot 3H_2O$.

	$[Sn^{IV}3,4,3\text{-LI}(1,2\text{-HOPO})]\cdot 3H_2O$
Chemical formula	$C_{34}H_{40}N_8O_{15}Sn$
Formula weight	919.42
Color, habit	Colorless, shard
Temperature (K)	100(2)
Crystal system	Orthorhombic
Space group	$C222_1$
a (Å)	16.0345(7)
b (Å)	17.0024(7)
c (Å)	13.3898(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3650.4(3)
Z	4
Density (Mg m^{-3})	1.673
F(000)	1880
Radiation Type	Synchrotron
μ (mm^{-1})	0.938
Crystal size (mm^3)	0.050 x 0.030 x 0.020
Meas. Refl.	31453
Indep. Refl.	8824
R(int)	0.0366
Final R indices	R = 0.0318
[I > 2σ(I)]	R_w = 0.0733
Goodness-of-fit	1.044
Absolute structure parameter	0.001(6)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.678, -0.910

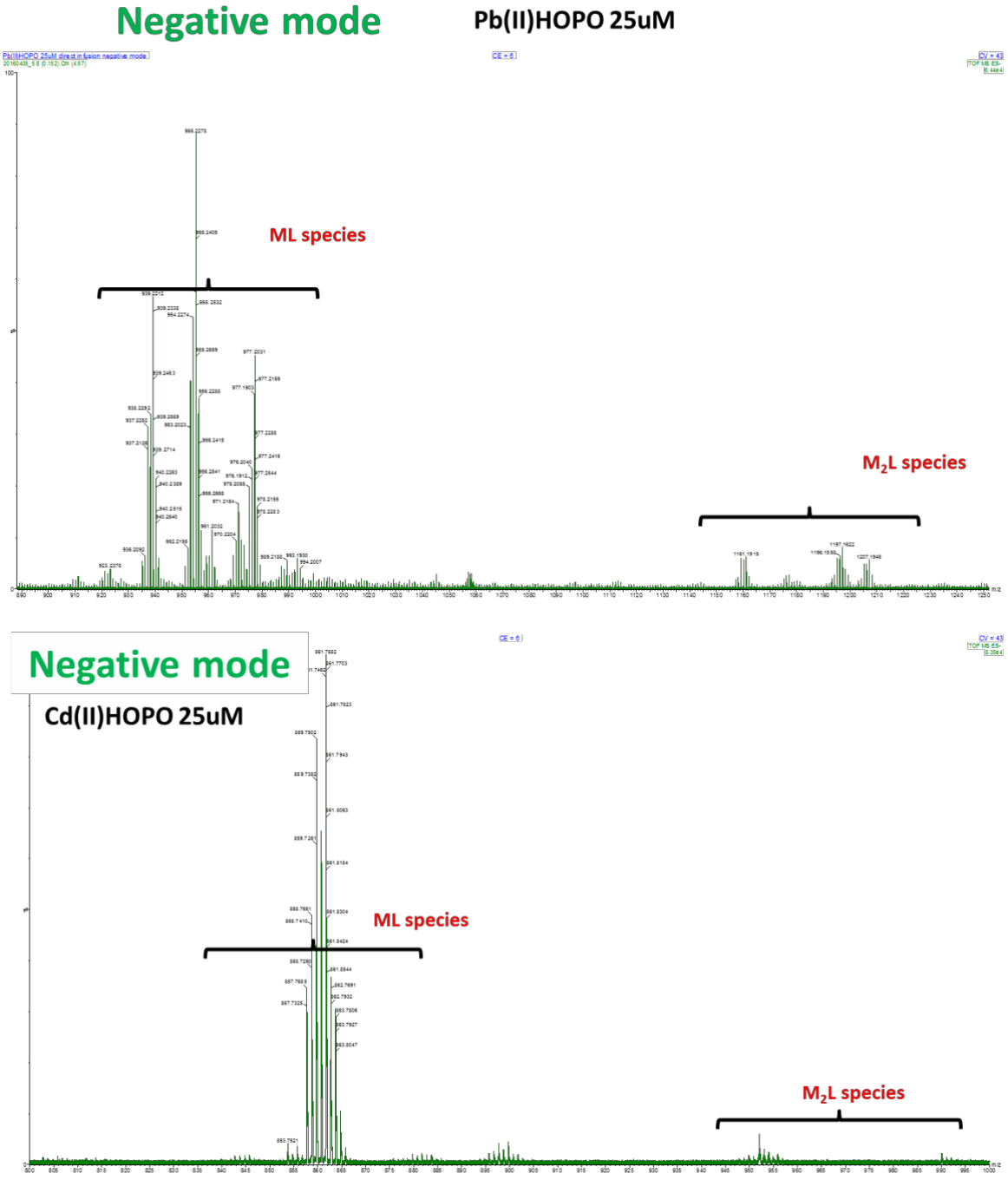

Figure S 6. High resolution mass spectrometry pattern of 3,4,3-LI(1,2-HOPO) aqueous samples containing 1 equivalent of Pb(II) or Cd(II). [Metal] = [3,4,3(LI-1,2-HOPO)] = 25 μM. Media: 0.5% formic acid in water. Ionization by electrospray. Negative mode.

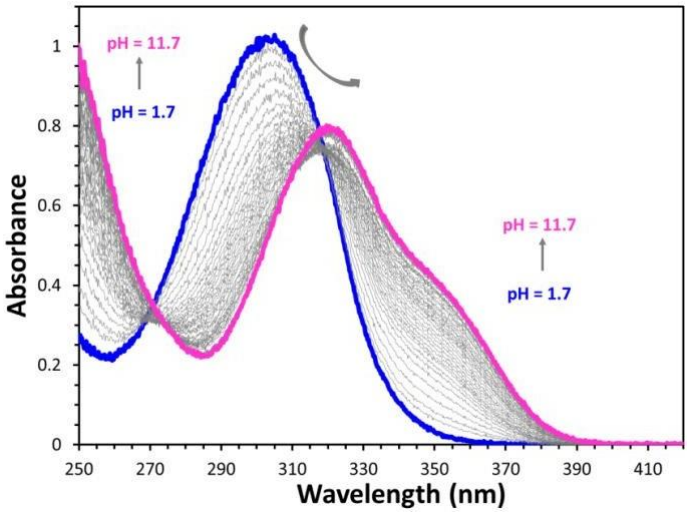

Figure S 7. Example of incremental spectrophotometric titration for the Cd(II)-3,4,3-LI(1,2-HOPO) system. 170 spectra measured between pH 1.2 and 11.7. [Cd] = [3,4,3-LI(1,2-HOPO)] = 55 µM. I = 0.1 M (KCl). Buffer: 5 mM CH3COOH, 5 mM CHES. T = 25ºC. Path length = 10 mm. Data abridged for clarity. Spectra corrected from the dilution induced by the addition of the titrant solution.

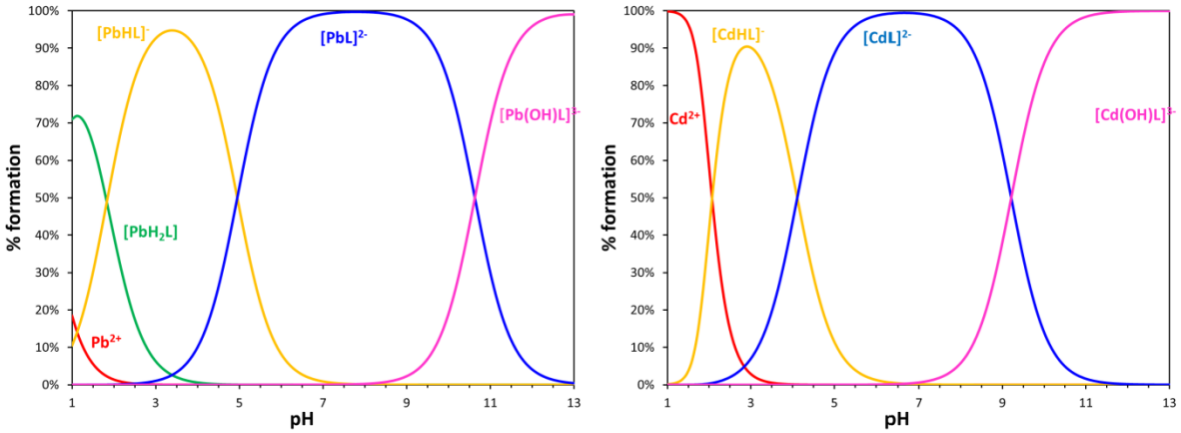

Figure S 8: Speciation diagram for the ligand 3,4,3-LI(1,2-HOPO) in the presence of 1 equivalent of Pb(II) **(left)** or 1 equivalent of Cd(II) **(right)**. T = 25ºC, I = 0.1M (KCl). L = 3,4,3-LI(1,2-HOPO)$^{4-}$. Hydrolysis constants of the metals were taken into account and set to the values found in the NIST standard reference database 46 at the corresponding ionic strength (Martell, A. E.; Smith, R. M.; Motekaitis, R. J.. National Institute of Standards and Technology: Gaithersburg, MD).

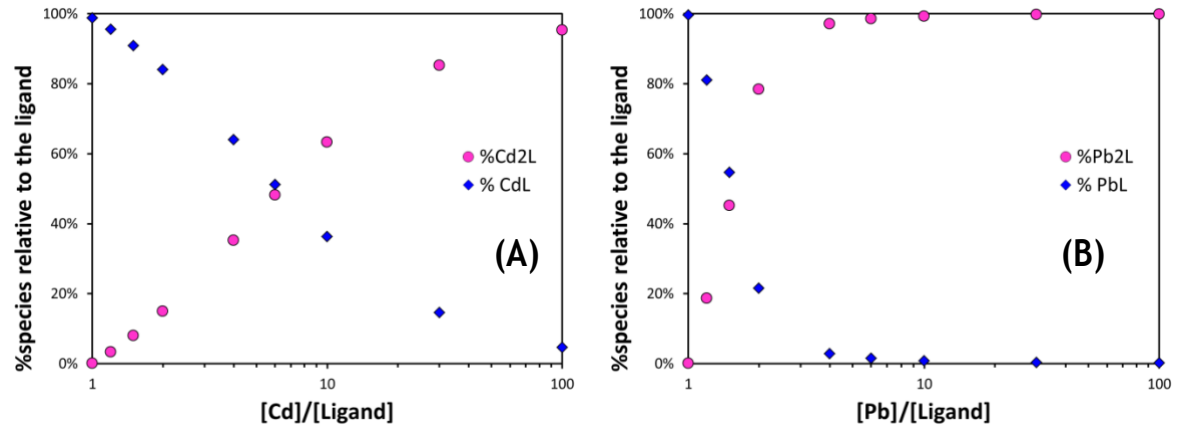

Figure S 9. Calculated distribution of the monomeric species (diamonds) and bimetallic species (circles) for the systems Cd(II)/3,4,3-LI(1,2-HOPO) **(left)** and Pb(II)/3,4,3-LI(1,2-HOPO) **(right)** as a function of the molar ratio $[metal]_{total}/[ligand]_{total}$. pH = 7.4, T = 25ºC, I = 0.1 M (KCl).

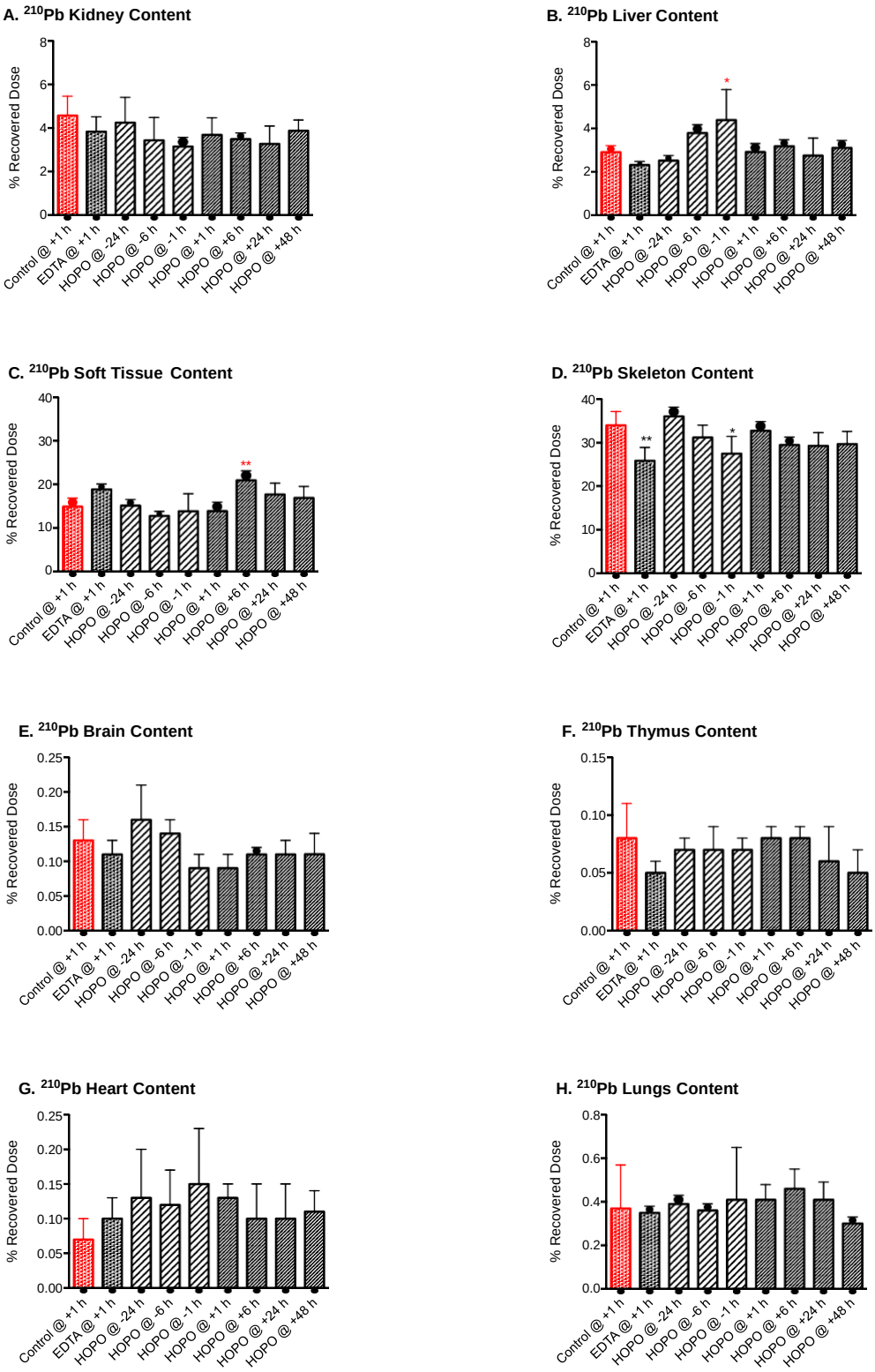

Figure S 10. Total ^{210}Pb content in kidneys (A), liver (B), soft tissues (C), skeleton (D), brain (E), thymus (F), heart (G), or lungs (H), at 4 days after metal challenge, preceded or followed by a single ip chelation treatment. Young adult female Swiss-Webster mice were injected iv with ^{210}Pb-citrate; saline or treatment (3,4,3-LI(1,2-HOPO) or Ca-ETDA [100 µmol/kg] was administered ip at 1 h, 6 h, or 24 h before or at 1 h, 6 h, 24 h, or 48 h after contamination; mice were euthanized 4 days after metal challenge. Data expressed as percent of recovered ^{210}Pb dose (% RD, mean ± SD) for each four-mouse group. Groups with significantly different retention than for control mice are indicated by * or ** ($p < 0.05$ or $p < 0.01$, 1-way ANOVA with post hoc Dunnett's multiple comparison test).

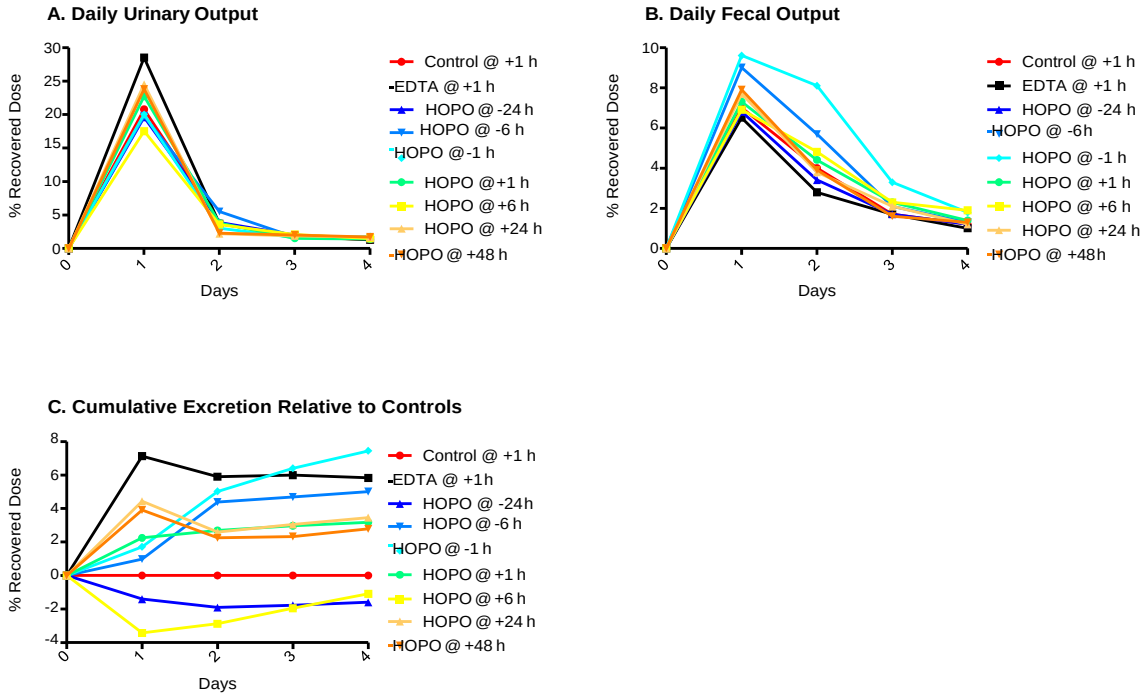

Figure S 11. Daily ^{210}Pb urinary (**A**) and fecal (**B**) output, as well as total ^{210}Pb cumulative excretion relative to control groups (**C**) at 4 days after a single ip chelation treatment. Young adult female Swiss-Webster mice were injected iv with ^{210}Pb-citrate; saline or treatment (3,4,3-LI(1,2-HOPO) or Ca-ETDA [100 µmol/kg] was administered ip at 1 h, 6 h, or 24 h before or at 1 h, 6 h, 24 h, or 48 h after contamination; mice were euthanized 4 days after metal challenge. Data expressed as percent of recovered ^{210}Pb dose (% RD, mean ± SD) for each four-mouse group.