

Supporting Information

The Reduction of Hg(II) by the Carbon Dioxide Radical Anion: A Theoretical and Experimental Investigation.

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The drinking water employed in some of the irradiation experiments (see inset of Figure 4) was groundwater from Manuel B. Gonnet (La Plata, Province of Buenos Aires, Argentina). The physico-chemical analysis of this water is summarized in Table S1.

Table S1: Physico-chemical analysis of the drinking water.

Parameter	Result	Units	Detection Limit	Method
Mercury	<0.0002	mg/L	0.0002	EPA SW 846 M 7470 EAA cold vapor
pH	7.4	U de pH	0.1	SM M 4500H-B-Potentiometric
Conductivity	1948	μohms/cm	1	SM M 2510B
Turbidity	<3	NTU	3	SM M 2130B-Nephelometric
Color	<3	Color units Pt-Co	3	SM M 2120B modified
Hardness	214	CaCO ₃ mg/L	1	SM M 2340C- EDTA Titration
Total alkalinity	537	CaCO ₃ mg/L	1	SM M 2320B-Titration
Calcium	46	mg/L	1	SM M 3500Ca-D- Titration
Magnesium	24	mg/L	1	SM M 3500Mg-E- Titration
Sodium	249	mg/L	1	SM M 3500Na-D- Flame photometry
Potassium	13	mg/L	1	SM M 3500K D Flame photometry
Carbonate	It does not contain	mg/L	1	SM M 2310B-Titration
Bicarbonate	656	mg/L	1	SM M 2310B-Titration
Chlorides	84	mg/L	1	SM M 4500Cl-B-Titration
Sulfates	83	mg/L	1	SM M 4500SO ₄ -E-Turbidimetry
Nitrates	34.2	mg/L	0.5	SM M 4500NO ₃ -E- UV Vis Spectrophotometry
Nitrites	0.014	mg/L	0.005	SM M 4500NO ₂ -B- UV Vis Spectrophotometry
Fluorides	0.55	mg/L	0.03	SM M 4500F-D- Spectrophotometry
Arsenic	0.02	mg/L	0.1	SM M 3500As-C- Spectrophotometry
Ammonium	0.2	mg/L	0.0002	SM M 4500NH ₃ -C- Spectrophotometry

Table S2. Comparison of some selected bond distances, in Å, of HgCl₂, Hg₂Cl₂ and Hg(H₂O)₆²⁺. Data from other sources are both experimental and calculated.

	Other source	Calc.
HgCl ₂	2.252 – linear (gas) ^a 2.38 – solid ^b	2.286 – linear (aqueous)
Hg ₂ Cl ₂	2.53 (Hg-Hg) ^b 2.43 (Hg-Cl) ^b	2.58 (Hg-Hg) (aqueous) 2.44 (Hg-Cl) (aqueous)
Hg(H ₂ O) ₆ ²⁺	2.37 (Hg-O) (aqueous) ^c	2.39 (Hg-O) (aqueous)

^a Taken from the 85th edition of the CRC Handbook of Chemistry and Physics.

^b AF Wells, *Structural Inorganic Chemistry*, 5th edition, Oxford Science Publications (1984)

^c Chillemi et al., *J Am Chem Soc* 129 (2007) 5430.

Table S3. Gibbs energies of formation for selected species considered in the present work. These were calculated according to Curtiss et al.,¹ in which several values involving standard states for the elements are taken from the literature. In the following table, experimental values were taken from the 85th edition of the CRC Handbook of Chemistry and Physics.

	ΔG_f^0 (kJ/mol)	
	Calc.	Exp.
HgCl ₂	-177.7	-178.6 ^a
Hg ₂ Cl ₂	-185.1	-210.7 ^a
HgCl ₅ ³⁻	-1645	-
CO ₂	-396.2	-394.4
CO ₂ ^{·-}	-610.9	-
Cl ⁻	-535.4	-541

^a Corresponds to solid state.

References

(1) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.