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--Supporting Information for: --

Nature of Hydride and Halide Encapsulation in Ag_8 Cages. Insights from Structural and Interaction Energy $[Ag_8(X)\{S_2P(O^iPr)_2\}_6]^+$ (X=H^-, F^-, Cl^-, Br^-, I^-) from Relativistic DFT Calculations

Raul Guajardo Maturana,[a] Alexandre O. Ortolan,[b] Peter. L. Rodríguez-Kessler,[c] Giovanni F. Caramori,[b] Renato L. T. Parreira[d] and Alvaro Muñoz-Castro[c*]

[a]*Universidad SEK, Facultad de Ciencias de la Salud, Instituto de Investigación Interdisciplinar en Ciencias Biomédicas SEK (I3CBSEK) Chile, Fernando Manterola 0789, Providencia, Santiago, Chile*

[b]*Departamento de Química, Universidade Federal de Santa Catarina, Campus Universitário Trindade, CP 476, Florianópolis, SC, 88040-900, Brazil.*

[c]*Laboratorio de Química Inorgánica y Materiales Moleculares, Facultad de Ingenieria, Universidad Autonoma de Chile, Llano Subercaceaux 2801, San Miguel, Santiago, Chile.*

[d]*Núcleo de Pesquisa em Ciências Exatas e Tecnológicas, Universidade de Franca, Franca, SP, 14404-600, Brazil.*

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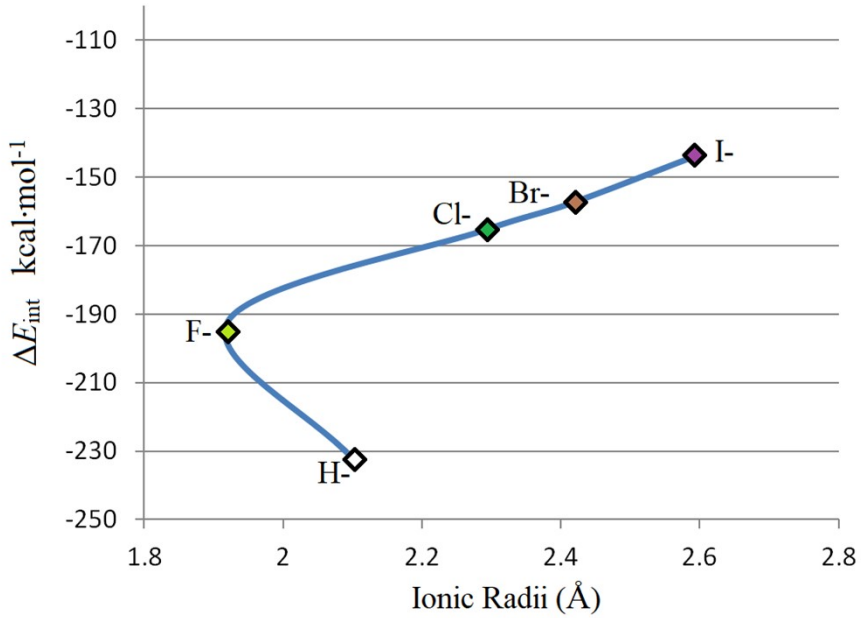

Figure S1. Comparison between ΔE_{int} in the formation of $[Ag_8(X)\{S_2P(OPr)_2\}_6]^+$ (X^- = H, **1**, F, **2**, Cl, **3**, Br, **4**, and, I, **5**) and the ionic radii for H-, F-, Cl-, Br-, and I-, as obtained from reference: Atomic and Ionic Radii of Elements 1–96, M. Rahm, R. Hoffmann, N. W. Ashcroft, *Chem. Eur. J.,* **2016**, 22, 14625-14632.

Table S1. Energy decomposition analysis for the $[Ag_8\{S_2P(OPr)_2\}_6]^{2+}$-$X^-$ interaction, values in kcal·mol^{-1}, at the **non-relativistic** BP86-D3 level of theory.

	1		**2**		**3**		**4**		**5**	
X=	H		F		Cl		Br		I	
ΔE_{Pauli}	421.2		74.2		155.0		211.0		281.7	
ΔE_{elstat}	-564.4	86.5%	-202.4	73.6%	-267.4	82.0%	-316.4	84.9%	-370.9	87.1%
ΔE_{orb}	-85.9	13.2%	-69.1	25.1%	-51.0	15.6%	-46.6	12.5%	-43.8	10.3%
ΔE_{disp}	-2.0	0.3%	-3.5	1.3%	-7.8	2.4%	-9.6	2.6%	-11.3	2.6%
ΔE_{int}	-231.0		-200.8		-171.4		-161.7		-144.2	
i-d%	91.0%		84.4%		77.0%		72.7%		68.4%	

Table S2. Energy decomposition analysis for the $[Ag_8\{S_2P(OPr)_2\}_6]^{2+}$-$X^-$ interaction, values in kcal·mol^{-1}, at the **relativistic** BP86-D3 level of theory as given at the main article, repeated here for easy comparison.

	1		**2**		**3**		**4**		**5**	
X=	H		F		Cl		Br		I	
ΔE_{Pauli}	427.2		75.2		157.2		213.9		276.0	
ΔE_{elstat}	-556.7	84.4% [a]	-190.6	71.3%	-257.5	79.8% [a]	-308.9	83.1% [a]	-357.5	85.1% [a]
ΔE_{orb}	-100.7	15.3% [a]	-73.2	27.4%	-57.3	17.8% [a]	-53.4	14.4% [a]	-51.5	12.3% [a]
ΔE_{disp}	-2.0	0.3% [a]	-3.5	1.3%	-7.8	2.4% [a]	-9.6	2.6% [a]	-11.3	2.7% [a]
ΔE_{int}	-232.2		-192.1		-165.5		-158.0		-144.2	
i-d%	90.7%		84.2%		76.6%		72.2%		68.6%	

Table S3. Energy decomposition analysis for the $[Ag_8\{S_2P(OPr)_2\}_6]^{2+}$-$X^-$ interaction, values in kcal·mol^{-1}, at the relativistic Hybrid **B3LYP-D3** level of theory.

	1		**2**		**3**		**4**		**5**	
X=	H		F		Cl		Br		I	
ΔE_{Pauli}	439.5		81.8		175.6		238.1		310.3	
ΔE_{elstat}	-571.6	85.5%	-199.8	73.6%	-268.6	79.7%	-321.7	82.5%	-375.7	84.2%
ΔE_{orb}	-93.6	14.0%	-65.2	24.0%	-53.6	15.9%	-49.5	12.7%	-47.5	10.6%
ΔE_{disp}	-3.0	0.5%	-6.3	2.3%	-14.9	4.4%	-18.9	4.9%	-22.8	5.1%
ΔE_{int}	-228.7		-189.5		-161.5		-152.1		-135.7	
i-d%	90.9%		85.1%		77.2%		72.5%		68.5%	

Table S4. Energy decomposition analysis for the $[Ag_8\{S_2P(OPr)_2\}_6]^{2+}$-$X^-$ interaction, values in kcal·mol^{-1}, at the relativistic Hybrid **PBE0-D3** level of theory.

	1		**2**		**3**		**4**		**5**	
X=	H		F		Cl		Br		I	
ΔE_{Pauli}	428.9		72.4		151.4		203.3		278.8	428.9
ΔE_{elstat}	-571.8	85.7%	-199.5	73.4%	-262.8	81.1%	-309.4	83.8%	-364.0	-571.8
ΔE_{orb}	-93.7	14.0%	-65.1	23.9%	-53.2	16.4%	-50.3	13.6%	-48.2	-93.7
ΔE_{disp}	-2.0	0.3%	-7.4	2.7%	-7.8	2.4%	-9.6	2.6%	-11.3	-2.0
ΔE_{int}	-238.6		-199.6		-172.4		-166.0		-144.7	
i-d%	90.6%		84.9%		77.1%		72.3%		69.2%	

Table S5. Energy decomposition analysis for the $[Ag_8\{S_2P(OPr)_2\}_6]^{2+}$-$X^-$ interaction, values in kcal·mol^{-1}, at the relativistic Meta-Hybrid M06-2X level of theory.

	1		**2**		**3**		**4**		**5**	
X=	H		F		Cl		Br		I	
ΔE_{Pauli}	432.9		183.1		159.0		213.5		263.7	183.1
ΔE_{elstat}	-570.4	89.2%	-312.7	87.4%	-266.2	85.0%	-313.3	84.6%	-353.0	-312.7
ΔE_{orb}	-69.0	10.8%	-45.2	12.6%	-47.0	15.0%	-57.1	15.4%	-43.9	-45.2
ΔE_{int}	-208.4		-174.7		-154.1		-156.9		-133.2	-174.7
i-d%	92.4%		91.2%		78.6%		73.4%		69.4%	