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ELECTRONIC SUPPLEMENTARY MATERIAL

On the dual character of charged metal-molecule hybrids and the opposite behaviour of the forward and reverse CT processes

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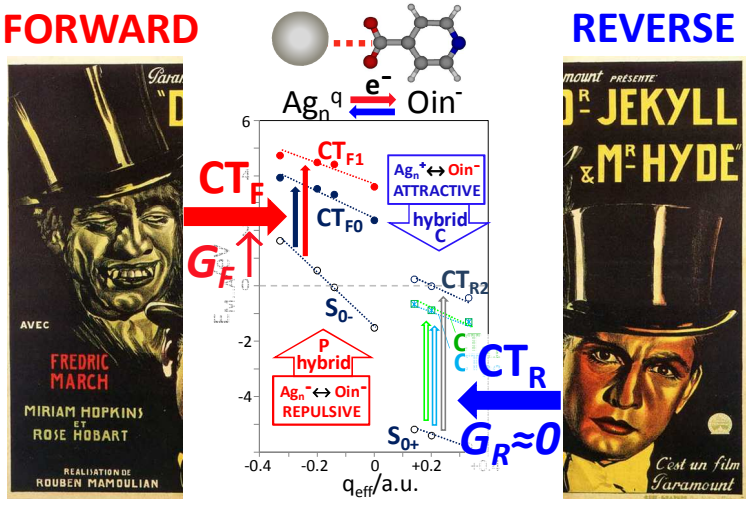

Computational details.

All the density functional theory (DFT) calculations have been carried out by using the Gaussian 09 suite of programs.[1] The geometry of the ground state (S_0) of each M-A system has been fully optimized with the only constrain of keeping the C_{2v} symmetry (see Fig. 1a) . Table S3 summarizes the corresponding Cartesian coordinates for the Ag-in$^-$ discussed complexes. Then, the singlet excited states have been obtained by means of time-dependent DFT (TDDFT) calculations.

Although in all the ground and excited states some amount of charge is donated from M to A or vice versa, the excited states with net transferred charges are easily recognized by comparing the Mulliken's charges of both moieties in the S_0 and the excited S_i states ($\Delta q_t = q_{A,Si} - q_{A,S0}$). Moreover, the corresponding single excitations of the CI expansion are checked in order to confirm the assignment. These CT states are characterized by significant Δq_t usually in the range 0.35-0.9 u.a., while the remaining non-CT excitations shows $\Delta q_t < 0.1$ a.u.

Concerning the theoretical description of the CT excited states, it is well established that DFT requires full Hartree-Fock exchange, what means that, for instance, widespread used functionals like the hybrid B3LYP[2] are not adequate given that systematically underestimate the energies of the CT transitions. This is the reason why we have used the long-range corrected M06-HF[3] and wB97X-D[4] functionals which have been proposed to specifically solve this problem. Anyway, quantitative theoretical prediction of the energies of CT states remains a challenge. Finally, the LanL2DZ[5] basis set is an standard effective core pseudopotential very often used as basis set in organometallic calculations.

The discussion in the manuscript has been centered on the M06-HF in order to be compared with our previous results.[6-8] Tables S1 and S2 summarizes the TDDFT M06-HF and wB97X-D results for the CT states of the Ag-Nin$^-$and Ag-Oin$^-$ complexes. This Table contains the corresponding root number, the respective vertical energies and symmetries,

the net donated charge in S_0 when the complex is formed ($\Delta q_{M\leftarrow A,S0}$) and the net transferred charges (Δq_t) in each CT state. Vertical excitation energies correspond to the difference between the respective energies of the ground S_0 and the CT states calculated without any structural rearrangement, i.e., by keeping unaltered the nuclear positions of the optimized S_0 geometry.

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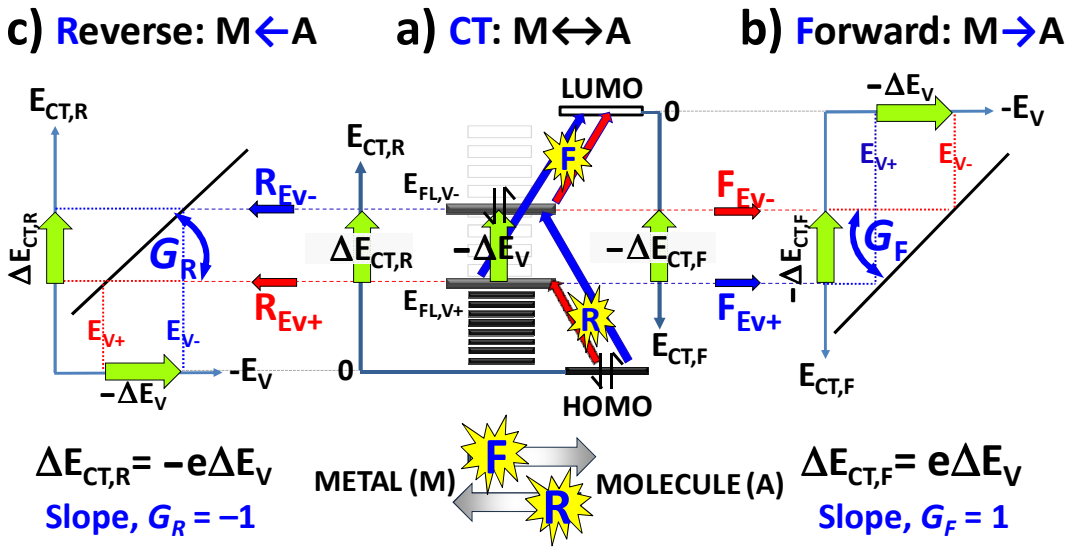

Scheme S1. Classical view of the effect of a negative shift of the electrode potential ($-\Delta E_V = E_{V-} - E_{V+}$) on the energy of the Fermi level of the metal ($\Delta E_{FL} = e\Delta E_V = E_{FL,V-} - E_{FL,V+}$) and on the CT energies, showing the equivalent red- and blue-shifts of the metal-to-molecule (M-A) CT transitions for the forward (F) and the reverse (R) processes, $-\Delta E_{CT,F} = \Delta E_{CT,R}$, respectively.

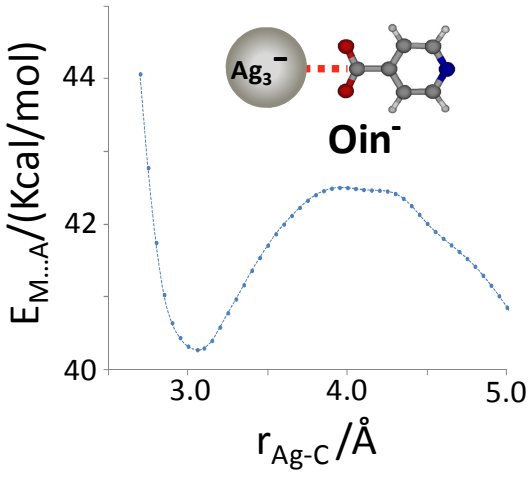

Figure S1. Dependence of the M06-HF/LanL2DZ bond energy ($E_{M...A}$/Kcal/mol) between the Ag_3^{-1} metallic cluster and the isonicotinate anion bonded through the carboxylate (Oin^-) on the Ag-C distance showing the metastable minimum at ca. 3 Å.

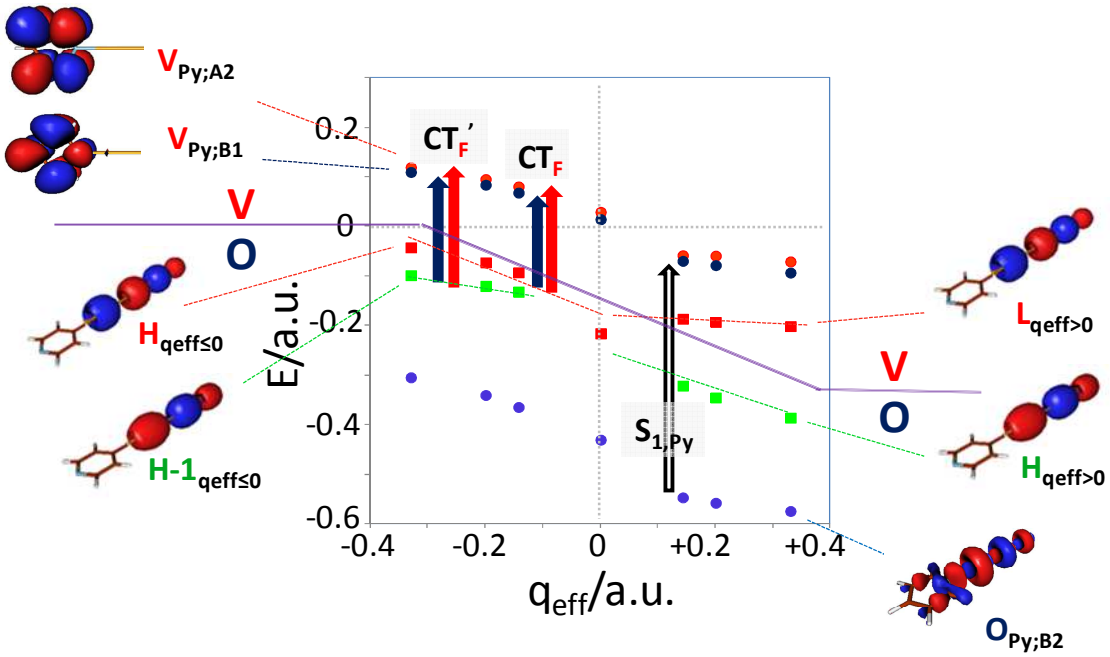

Figure S2. Dependence on q_{eff} of the M06-HF/LanL2DZ energies (E) of the occupied (O) and virtual (V) molecular orbitals of the $[Ag_n\text{-}Py]^q$ complex involved in the CT transitions. H, L and H-1 refers to the HOMO, LUMO and HOMO-1 orbitals of silver clusters at $q_{eff}\leq 0$ or $q_{eff}>0$, respectively (only orbitals of the Ag_7 cluster are drawn). V_{Py} and $O_{PY;B2}$ are the corresponding virtual and occupied orbitals of pyridine involved in the forward CT transition and in the $S_0\text{-}S_{1,Py}$ excitation of pyridine, respectively. It can be see that the orbitals related to the secondary CT_F' series (H-1→V_{PY}) shows lesser dependence on q_{eff} than the main CT_F (H→V_{PY}) one, so explaining its very small slope *S* (eq. 1). Moreover, only a CT_F series survives at $q_{eff}>0$ given that the HOMO orbital at $q_{eff}\leq 0$ is empty at positive charges and cannot by the origin of any forward CT transition.

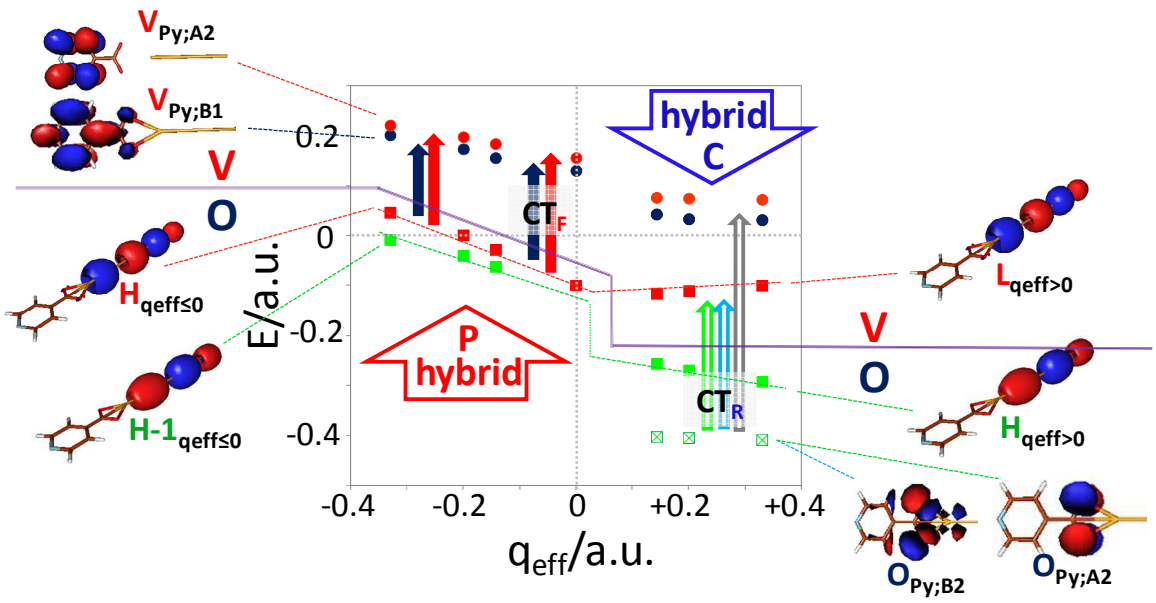

Figure S3. Dependence on q_{eff} of the M06-HF/LanL2DZ energies (E) of the occupied (O) and virtual (V) molecular orbitals of the $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ complex involved in the CT transitions. H, L and H-1 refers to the HOMO, LUMO and HOMO-1 orbitals of silver clusters at $q_{eff}\leq 0$ or $q_{eff}>0$, respectively (only orbitals of the Ag_7 cluster are drawn). V_{PY} and O_{PY} are the corresponding virtual and occupied orbitals of isonicotinate involved in the forward and reverse CT excitations, respectively. The dual character of the electronic structure of this hybrid is related to the significant gap of the HOMO when q_{eff} changes from negative to positive values. This gap can be also appreciated in the case of the Ag-Py complex (Fig. S1) but the transition is much smoother.

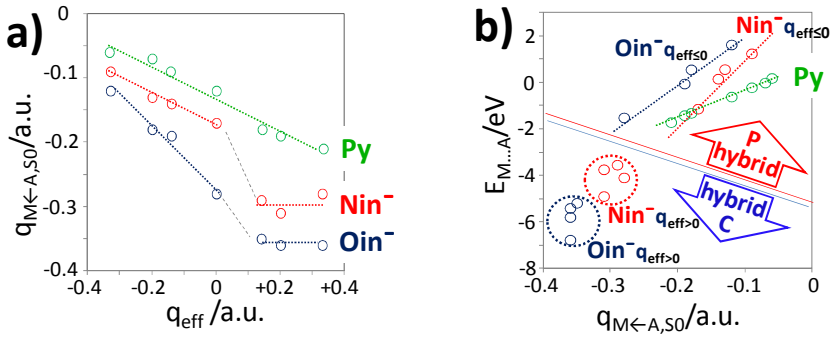

Figure S4. a) M06-HF/LanL2DZ Mulliken charges donated from the molecule (A) to the metal cluster (M) ($q_{M\leftarrow A,S0}$=-$q_{Py,S0}$) in the corresponding S_0 ground state of the complexes formed by pyridine (Py) or isonicotinate anion bonded to silver clusters through the nitrogen (Py and Nin$^-$) or the carboxylate (Oin$^-$) versus q_{eff}. b) Correlation between the strength of the M-A bond ($E_{M...A}$) in S_0 and the donated charge in the respective ground states $q_{M\leftarrow A,S0}$ of the three kind of complexes showing the differentiated dependence of P- and C-hybrids.

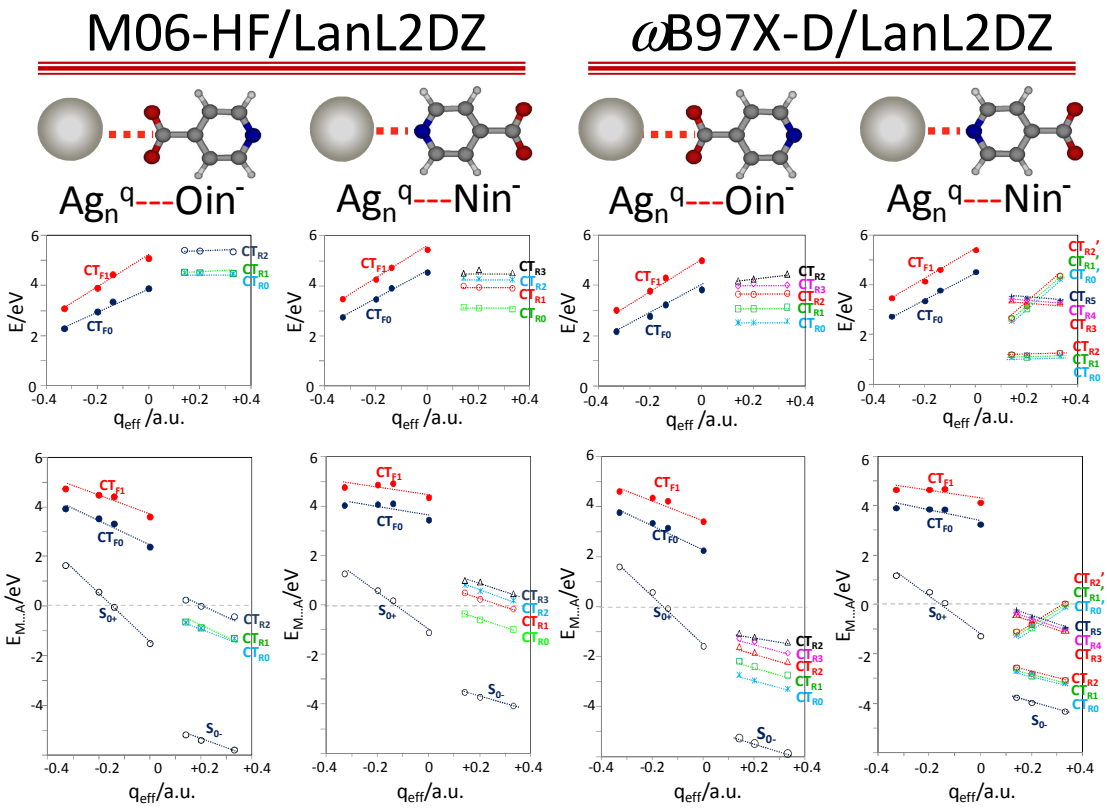

Figure S5. Dependence on q_{eff} of the M06-HF and wB97X-D/LanL2DZ energies (E, upper) of the ground (S_0) and the forward (CT_{Fi}) and reverse (CT_{Ri}) charge transfer states of isonicotinate (in$^-$) bonded to silver clusters (Ag_n^q) through the aromatic nitrogen (Ag-Nin$^-$) or the carboxylate (Ag-Oin$^-$). Energies of the same states but referred to the energy of the respective metallic clusters and the adsorbate at infinite separation ($E_{M...A}$, bottom).

Table S1.- Time dependent M06-HF/LanL2DZ results for $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ and $[(Ag_n)^q\text{-}Nin^-]^{q-1}$ complexes: donated charge in the ground S_0 state ($q_{M\leftarrow A,S0}$) and transferred charge Δq_t, energies and symmetries of the roots (S_i) corresponding to the forward (Ag →in) and reverse (in→Ag) CT_{Fi} and CT_{Ri} excited states.

		$[(Ag_n)^q\text{-}Oin^-]^{q-1}$			$[(Ag_n)^q\text{-}Nin^-]^{q-1}$			CT
Complex	q_{eff}	$q_{M\leftarrow A,S0}$	Δq_t	**CT states**	Δq_t	**CT states**	$q_{M\leftarrow A,S0}$	**direction**
Ag_3^--in^-	-0.33	-0.12	-0.76	S_4=2.28eV (CT_{F0}),B_1	-0.74	S_4=2.76eV (CT_{F0}),B_1	-0.09	Ag →in
			-0.89	S_8=3.08eV (CT_{F1}),A_2	-0.85	S_{12}=3.49eV (CT_{F1}),A_2		
Ag_5^--in^-	-0.20	-0.18	-0.58	S_7=2.95eV (CT_{F0}),B_1	-0.73	S_{11}=3.48eV (CT_{F0}),B_1	-0.13	Ag →in
			-0.87	S_{20}=3.90eV (CT_{F1}),A_2	-0.83	S_{20}=4.27eV (CT_{F1}),A_2		
Ag_7^--in^-	-0.14	-0.19	-0.35	S_{11}=3.35eV (CT_{F0}),B_1	-0.52	S_{20}=3.92eV (CT_{F0}),B_1	-0.14	Ag →in
			-0.84	S_{32}=4.44eV(CT_{F1}),A_2	-0.84	S_{38}=4.74eV (CT_{F1}),A_2		
Ag_2-in^-	0.00	-0.28	-0.43	S_4=3.88eV (CT_{F0}),B_1	-0.60	S_8=4.55eV (CT_{F0}),B_1	-0.17	Ag →in
			-0.90	S_{11}=5.09eV (CT_{F1}),A_2	-0.77	S_{12}=5.46eV (CT_{F1}),A_2		
Ag_7^+-in^-	+0.14	-0.35	+0.34	S_{16}=4.52eV (CT_{R0}),B_2	+0.83	S_5=3.17eV (CT_{R0}),A_2	-0.29	in→Ag
			+0.45	S_{17}=4.54eV (CT_{R1}),A_2	+0.79	S_{14}=4.02eV (CT_{R1}),A_1		
			+0.25	S_{30}=5.42eV (CT_{R2}),A_1	+0.79	S_{16}=4.34eV (CT_{R2}),B_2		
					+0.83	S_{20}=4.52eV (CT_{R3}),A_2		
Ag_5^+-in^-	+0.20	-0.36	+0.49	S_{10}=4.52eV (CT_{R0}),A_2	+0.79	S_3=3.13eV (CT_{R0}),A_2	-0.31	in→Ag
			+0.39	S_{11}=4.52eV (CT_{R1}),B_2	+0.77	S_9=3.96eV (CT_{R1}),A_1		
			+0.25	S_{18}=5.39eV (CT_{R2}),A_1	+0.78	S_{11}=4.30eV (CT_{R2}),B_2		
					+0.75	S_{15}=4.66eV (CT_{R3}),A_2		
Ag_3^+-in^-	+0.33	-0.36	+0.54	S_6=4.49eV (CT_{R0}),A_2	+0.83	S_2=3.10eV (CT_{R0}),A_2	-0.28	in→Ag
			+0.41	S_7=4.49eV (CT_{R1}),B_2	+0.81	S_4=3.92eV (CT_{R1}),A_1		
			+0.24	S_{11}=5.36eV(CT_{R2}),A_1	+0.87	S_8=4.27eV (CT_{R2}),B_2		
					+0.78	S_{10}=4.54eV (CT_{R3}),A_2		

Table S2.- Time dependent wB97X-D/LanL2DZ results for $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ and $[(Ag_n)^q\text{-}Nin^-]^{q-1}$ complexes: donated charge in the ground S_0 state ($q_{M\leftarrow A,S0}$) and transferred charge Δq_t, energies and symmetries of the roots (S_i) corresponding to the forward (Ag →in) and reverse (in→Ag) CT_{Fi} and CT_{Ri} excited states.

		$[(Ag_n)^q\text{-}Oin^-]^{q-1}$			$[(Ag_n)^q\text{-}Nin^-]^{q-1}$			CT
Complex	q_{eff}	$q_{M\leftarrow A,S0}$	Δq_t	**CT states**	Δq_t	**CT states**	$q_{M\leftarrow A,S0}$	**direction**
Ag_3^--in^-	-0.33	-0.16	-0.73	S_3=2.17eV (CT_{F0}),B_1	-0.68	S_4=2.73eV (CT_{F0}),B_1	-0.13	Ag →in
			-0.82	S_7=3.02eV (CT_{F1}),A_2	-0.80	S_8=3.47eV (CT_{F1}),A_2		
Ag_5^--in^-	-0.20	-0.22	-0.42	S_4=2.77eV (CT_{F0}),B_1	-0.69	S_8=3.35eV (CT_{F0}),B_1	-0.15	Ag →in
			-0.81	S_{12}=3.78eV (CT_{F1}),A_2	-0.79	S_{17}=4.14eV (CT_{F1}),A_2		
Ag_7^--in^-	-0.14	-0.23	-0.51	S_9=3.23eV (CT_{F0}),B_1	-0.60	S_{15}=3.78eV (CT_{F0}),B_1	-0.18	Ag →in
			-0.79	S_{24}=4.30eV(CT_{F1}),A_2	-0.80	S_{34}=4.61eV (CT_{F1}),A_2		
Ag_2-in^-	0.00	-0.27	-0.62	S_4=3.83eV (CT_{F0}),B_1	-0.67	S_7=4.52eV (CT_{F0}),B_1	-0.22	Ag →in
			-0.73	S_{11}=4.99eV (CT_{F1}),A_2	-0.73	S_{21}=5.40eV (CT_{F1}),A_2		
Ag_7^+-in^-	+0.14	-0.43	+0.47	S_3=2.53eV (CT_{R0}),B_2	+0.79	S_1=1.08eV (CT_{R0}),B_2	-0.34	in→Ag
			+0.59	S_6=3.08eV (CT_{R1}),A_2	+0.79	S_2=1.19eV (CT_{R1}),A_2		
			+0.31	S_8=3.66eV (CT_{R2}),A_1	+0.80	S_3=1.22eV (CT_{R2}),A_1		
			+0.52	S_{12}=3.98eV (CT_{R3}),A_1	+0.80	S_7=2.54eV ($CT_{R0'}$),B_2		
			+0.74	S_{21}=4.19eV (CT_{R4}),A_2	+0.80	S_8=2.64eV ($CT_{R1'}$),A_2		
					+0.79	S_9=2.68eV ($CT_{R2'}$),A_1		
					+0.64	S_{14}=3.38eV (CT_{R3}),B_1		
					+0.73	S_{15}=3.44eV (CT_{R4}),A_2		
					+0.18	S_{17}=3.55eV (CT_{R5}),A_1		
Ag_5^+-in^-	+0.20	-0.44	+0.44	S_2=2.53eV (CT_{R0}),B_2	+0.79	S_1=1.08eV (CT_{R0}),A_2	-0.34	in→Ag
			+0.59	S_4=3.08eV (CT_{R1}),A_2	+0.79	S_2=1.18eV (CT_{R1}),A_1		
			+0.27	S_6=3.65eV (CT_{R2}),A_1	+0.78	S_3=1.20eV (CT_{R2}),B_2		
			+0.57	S_{10}=4.08eV (CT_{R3}),A_1	+0.79	S_8=3.03eV ($CT_{R2'}$),A_1		
			+0.74	S_{16}=4.26eV (CT_{R4}),A_2	+0.79	S_9=3.13eV($CT_{R3'}$),B_2		
					+0.79	S_{10}=3.16eV ($CT_{R1'}$),A_2		
					+0.64	S_{12}=3.33eV(CT_{R3}),B_1		
					+0.75	S_{13}=3.38eV (CT_{R4}),A_2		
					+0.22	S_{15}=3.48eV (CT_{R5}),A_1		
Ag_3^+-in^-	+0.33	-0.44	+0.46	S_2=2.59eV (CT_{R0}),B_2	+0.77	S_1=1.15eV (CT_{R0}),B_2	-0.35	in→Ag
			+0.59	S_3=3.14eV (CT_{R1}),A_2	+0.78	S_2=1.26eV (CT_{R1}),A_2		
			+0.19	S_4=3.69eV(CT_{R2}),A_1	+0.76	S_3=1.27eV (CT_{R2}),A_1		
			+0.27	S_6=4.02eV(CT_{R3}),A_1	+0.62	S_7=3.31eV (CT_{R3}),B_1		
			+0.73	S_{11}=4.46eV (CT_{R4}),A_2	+0.72	S_8=3.34eV(CT_{R4}),A_2		
					+0.24	S_{10}=3.38eV(CT_{R5}),A_1		
					+0.81	S_{18}=4.24eV($CT_{R0'}$),B_2		
					+0.82	S_{21}=4.35eV($CT_{R1'}$),A_2		
					+0.85	S_{22}=4.37eV($CT_{R2'}$),A_1		

Table S3.- M06-HF/LanL2DZ and wB97X-D optimized geometries for the ground S_0 state of the $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ and $[(Ag_n)^q\text{-}Nin^-]^{q-1}$ complexes.

M06-HF/LanL2DZ Optimized geometries of $[(Ag_n)^q\text{-}Nin^-]^{q-1}$

$[(Ag_3)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.520007
C	0.000000	1.173492	1.835184
C	0.000000	-1.173492	1.835184
C	0.000000	1.209247	0.441953
C	0.000000	-1.209247	0.441953
C	0.000000	0.000000	-0.268153
H	0.000000	2.084430	2.420189
H	0.000000	-2.084430	2.420189
H	0.000000	2.133911	-0.122388
H	0.000000	-2.133911	-0.122388
C	0.000000	0.000000	-1.816413
O	0.000000	-1.160366	-2.329641
O	0.000000	1.160366	-2.329641
Ag	0.000000	0.000000	4.690571
Ag	0.000000	0.000000	7.618447
Ag	0.000000	0.000000	10.324789

$[(Ag_5)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.423871
C	0.000000	1.172885	1.738981
C	0.000000	-1.172885	1.738981
C	0.000000	1.208974	0.345455
C	0.000000	-1.208974	0.345455
C	0.000000	0.000000	-0.364958
H	0.000000	2.083420	2.324586
H	0.000000	-2.083420	2.324586
H	0.000000	2.133879	-0.218249
H	0.000000	-2.133879	-0.218249
C	0.000000	0.000000	-1.913043
O	0.000000	-1.159957	-2.427712
O	0.000000	1.159957	-2.427712
Ag	0.000000	0.000000	4.600113
Ag	0.000000	0.000000	7.494233
Ag	0.000000	0.000000	10.227856
Ag	0.000000	0.000000	13.183876
Ag	0.000000	0.000000	15.881774

$[(Ag_7)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.281950
C	0.000000	1.172582	1.597054
C	0.000000	-1.172582	1.597054
C	0.000000	1.208825	0.203342
C	0.000000	-1.208825	0.203342
C	0.000000	0.000000	-0.507220
H	0.000000	2.082947	2.182939
H	0.000000	-2.082947	2.182939
H	0.000000	2.133890	-0.360035
H	0.000000	-2.133890	-0.360035
C	0.000000	0.000000	-2.055136
O	0.000000	-1.159786	-2.570610
O	0.000000	1.159786	-2.570610
Ag	0.000000	0.000000	4.461063
Ag	0.000000	0.000000	7.340758
Ag	0.000000	0.000000	10.086459
Ag	0.000000	0.000000	13.012540
Ag	0.000000	0.000000	15.733875
Ag	0.000000	0.000000	18.703215
Ag	0.000000	0.000000	21.396958

$[(Ag_2)^0\text{-}Nin^-]^{-1}$

N	0.000000	0.000000	2.548120
C	0.000000	1.166894	1.863172
C	0.000000	-1.166894	1.863172
C	0.000000	1.206151	0.465837
C	0.000000	-1.206151	0.465837
C	0.000000	0.000000	-0.248417
H	0.000000	2.073499	2.455204
H	0.000000	-2.073499	2.455204
H	0.000000	2.134429	-0.091041
H	0.000000	-2.134429	-0.091041
C	0.000000	0.000000	-1.793695
O	0.000000	-1.156299	-2.324603
O	0.000000	1.156299	-2.324603
Ag	0.000000	0.000000	4.808870
Ag	0.000000	0.000000	7.507829

$[(Ag_7)^{-1}\text{-}Nin^-]^{-2}$

N	0.000000	0.000000	2.205419
C	0.000000	1.166188	1.521244
C	0.000000	-1.166188	1.521244
C	0.000000	1.205785	0.122925
C	0.000000	-1.205785	0.122925
C	0.000000	0.000000	-0.592178
H	0.000000	2.071754	2.114949
H	0.000000	-2.071754	2.114949
H	0.000000	2.135069	-0.432122
H	0.000000	-2.135069	-0.432122
C	0.000000	0.000000	-2.136951
O	0.000000	-1.155351	-2.672235
O	0.000000	1.155351	-2.672235
Ag	0.000000	0.000000	4.515410
Ag	0.000000	0.000000	7.228914
Ag	0.000000	0.000000	10.347570
Ag	0.000000	0.000000	13.102692
Ag	0.000000	0.000000	16.023349
Ag	0.000000	0.000000	18.889046
Ag	0.000000	0.000000	21.667049

$[(Ag_5)^{-1}\text{-}Nin^-]^{-2}$

N	0.000000	0.000000	2.355847
C	0.000000	1.165089	1.671837
C	0.000000	-1.165089	1.671837
C	0.000000	1.205364	0.272657
C	0.000000	-1.205364	0.272657
C	0.000000	0.000000	-0.443326
H	0.000000	2.069739	2.267109
H	0.000000	-2.069739	2.267109
H	0.000000	2.135368	-0.281077
H	0.000000	-2.135368	-0.281077
C	0.000000	0.000000	-1.987704
O	0.000000	-1.154606	-2.526298
O	0.000000	1.154606	-2.526298
Ag	0.000000	0.000000	4.705378
Ag	0.000000	0.000000	7.430377
Ag	0.000000	0.000000	10.561119
Ag	0.000000	0.000000	13.397759
Ag	0.000000	0.000000	16.231939

$[(Ag_3)^{-1}\text{-}Nin^{-}]^{-2}$

N	0.000000	0.000000	2.475638
C	0.000000	1.163170	1.791672
C	0.000000	-1.163170	1.791672
C	0.000000	1.204725	0.390956
C	0.000000	-1.204725	0.390956
C	0.000000	0.000000	-0.326577
H	0.000000	2.066124	2.389946
H	0.000000	-2.066124	2.389946
H	0.000000	2.135854	-0.160836
H	0.000000	-2.135854	-0.160836
C	0.000000	0.000000	-1.870175
O	0.000000	-1.153406	-2.414409
O	0.000000	1.153406	-2.414409
Ag	0.000000	0.000000	4.908336
Ag	0.000000	0.000000	7.706615
Ag	0.000000	0.000000	10.671349

M06-HF/LanL2DZ Optimized geometries of $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ systems

$[(Ag_3)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.558225
C	0.000000	1.161068	1.872675
C	0.000000	-1.161068	1.872675
C	0.000000	1.209517	0.471345
C	0.000000	-1.209517	0.471345
C	0.000000	0.000000	-0.233007
H	0.000000	2.065766	2.465785
H	0.000000	-2.065766	2.465785
H	0.000000	2.147419	-0.068373
H	0.000000	-2.147419	-0.068373
C	0.000000	0.000000	-1.735037
O	0.000000	-1.120041	-2.370529
O	0.000000	1.120041	-2.370529
Ag	0.000000	0.000000	-4.419501
Ag	0.000000	0.000000	-7.432969
Ag	0.000000	0.000000	-10.119674

$[(Ag_5)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.668759
C	0.000000	1.161016	1.983060
C	0.000000	-1.161016	1.983060
C	0.000000	1.209419	0.581742
C	0.000000	-1.209419	0.581742
C	0.000000	0.000000	-0.122776
H	0.000000	2.065759	2.576114
H	0.000000	-2.065759	2.576114
H	0.000000	2.147173	0.041768
H	0.000000	-2.147173	0.041768
C	0.000000	0.000000	-1.625199
O	0.000000	-1.120198	-2.259850
O	0.000000	1.120198	-2.259850
Ag	0.000000	0.000000	-4.312454
Ag	0.000000	0.000000	-7.302997
Ag	0.000000	0.000000	-10.002929
Ag	0.000000	0.000000	-13.000319
Ag	0.000000	0.000000	-15.687912

$[(Ag_7)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.818243
C	0.000000	1.160986	2.132454
C	0.000000	-1.160986	2.132454
C	0.000000	1.209372	0.731125
C	0.000000	-1.209372	0.731125
C	0.000000	0.000000	0.026524
H	0.000000	2.065763	2.725482
H	0.000000	-2.065763	2.725482
H	0.000000	2.147048	0.190997
H	0.000000	-2.147048	0.190997
C	0.000000	0.000000	-1.476150
O	0.000000	-1.120288	-2.110300
O	0.000000	1.120288	-2.110300
Ag	0.000000	0.000000	-4.164825
Ag	0.000000	0.000000	-7.143431
Ag	0.000000	0.000000	-9.847649
Ag	0.000000	0.000000	-12.822126
Ag	0.000000	0.000000	-15.524721
Ag	0.000000	0.000000	-18.529240
Ag	0.000000	0.000000	-21.216299

$[(Ag_2)^0\text{-}Oin^-]^{-1}$

N	0.000000	0.000000	2.542723
C	0.000000	1.159398	1.851825
C	0.000000	-1.159398	1.851825
C	0.000000	1.206395	0.450465
C	0.000000	-1.206395	0.450465
C	0.000000	0.000000	-0.260239
H	0.000000	2.065853	2.443471
H	0.000000	-2.065853	2.443471
H	0.000000	2.140067	-0.097125
H	0.000000	-2.140067	-0.097125
C	0.000000	0.000000	-1.778548
O	0.000000	-1.132103	-2.374629
C	0.000000	1.132103	-2.374629
Ag	0.000000	0.000000	-4.616850
Ag	0.000000	0.000000	-7.375255

$[(Ag_7)^{-1}\text{-}Oin^-]^{-2}$

N	0.000000	0.000000	2.918245
C	0.000000	1.159327	2.226812
C	0.000000	-1.159327	2.226812
C	0.000000	1.206319	0.825491
C	0.000000	-1.206319	0.825491
C	0.000000	0.000000	0.114528
H	0.000000	2.066041	2.818157
H	0.000000	-2.066041	2.818157
H	0.000000	2.139621	0.277128
H	0.000000	-2.139621	0.277128
C	0.000000	0.000000	-1.404571
O	0.000000	-1.132280	-1.999637
O	0.000000	1.132280	-1.999637
Ag	0.000000	0.000000	-4.254639
Ag	0.000000	0.000000	-7.033690
Ag	0.000000	0.000000	-10.131716
Ag	0.000000	0.000000	-12.884220
Ag	0.000000	0.000000	-15.883563
Ag	0.000000	0.000000	-18.733451
Ag	0.000000	0.000000	-21.542983

$[(Ag_5)^{-1}\text{-}Oin^-]^{-2}$

N	0.000000	0.000000	2.783689
C	0.000000	1.159020	2.091164
C	0.000000	-1.159020	2.091164
C	0.000000	1.205768	0.689815
C	0.000000	-1.205768	0.689815
C	0.000000	0.000000	-0.022565
H	0.000000	2.066098	2.682268
H	0.000000	-2.066098	2.682268
H	0.000000	2.138302	0.139979
H	0.000000	-2.138302	0.139979
C	0.000000	0.000000	-1.545401
O	0.000000	-1.134733	-2.132695
O	0.000000	1.134733	-2.132695
Ag	0.000000	0.000000	-4.425911
Ag	0.000000	0.000000	-7.202986
Ag	0.000000	0.000000	-10.513868
Ag	0.000000	0.000000	-13.340781
Ag	0.000000	0.000000	-16.213395

[$(Ag_3)^{-1}$-Oin^-]$^{-2}$

N	0.000000	0.000000	2.650603
C	0.000000	1.158426	1.955867
C	0.000000	-1.158426	1.955867
C	0.000000	1.204596	0.554450
C	0.000000	-1.204596	0.554450
C	0.000000	0.000000	-0.161283
H	0.000000	2.066245	2.546543
H	0.000000	-2.066245	2.546543
H	0.000000	2.135699	0.001914
H	0.000000	-2.135699	0.001914
C	0.000000	0.000000	-1.694277
O	0.000000	-1.143009	-2.259507
O	0.000000	1.143009	-2.259507
Ag	0.000000	0.000000	-4.752612
Ag	0.000000	0.000000	-7.579715
Ag	0.000000	0.000000	-10.701407

wB97XD/LanL2DZ Optimized geometries of $[(Ag_n)^q\text{-}Nin^-]^{q-1}$ systems

$[(Ag_3)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.556081
C	0.000000	1.176237	1.862197
C	0.000000	-1.176237	1.862197
C	0.000000	1.207335	0.471425
C	0.000000	-1.207335	0.471425
C	0.000000	0.000000	-0.248847
H	0.000000	2.089289	2.446289
H	0.000000	-2.089289	2.446289
H	0.000000	2.134575	-0.090264
H	0.000000	-2.134575	-0.090264
C	0.000000	0.000000	-1.799363
O	0.000000	-1.163742	-2.320640
O	0.000000	1.163742	-2.320640
Ag	0.000000	0.000000	4.701045
Ag	0.000000	0.000000	7.490467
Ag	0.000000	0.000000	10.122445

$[(Ag_5)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.502076
C	0.000000	1.175392	1.807704
C	0.000000	-1.175392	1.807704
C	0.000000	1.206995	0.416609
C	0.000000	-1.206995	0.416609
C	0.000000	0.000000	-0.303932
H	0.000000	2.088213	2.392183
H	0.000000	-2.088213	2.392183
H	0.000000	2.134510	-0.144520
H	0.000000	-2.134510	-0.144520
C	0.000000	0.000000	-1.854219
O	0.000000	-1.163428	-2.376743
O	0.000000	1.163428	-2.376743
Ag	0.000000	0.000000	4.652400
Ag	0.000000	0.000000	7.419536
Ag	0.000000	0.000000	10.072178
Ag	0.000000	0.000000	12.877128
Ag	0.000000	0.000000	15.504210

$[(Ag_7)^{+1}\text{-}Nin^-]^0$

N	0.000000	0.000000	2.415918
C	0.000000	1.174974	1.721332
C	0.000000	-1.174974	1.721332
C	0.000000	1.206825	0.330042
C	0.000000	-1.206825	0.330042
C	0.000000	0.000000	-0.390648
H	0.000000	2.087690	2.305995
H	0.000000	-2.087690	2.305995
H	0.000000	2.134496	-0.230785
H	0.000000	-2.134496	-0.230785
C	0.000000	0.000000	-1.940839
O	0.000000	-1.163256	-2.464075
O	0.000000	1.163256	-2.464075
Ag	0.000000	0.000000	4.569267
Ag	0.000000	0.000000	7.325907
Ag	0.000000	0.000000	9.985325
Ag	0.000000	0.000000	12.769761
Ag	0.000000	0.000000	15.417791
Ag	0.000000	0.000000	18.229260
Ag	0.000000	0.000000	20.853084

$[(Ag_2)^0\text{-}Nin^-]^{-1}$

N	0.000000	0.000000	2.569717
C	0.000000	1.167180	1.871764
C	0.000000	-1.167180	1.871764
C	0.000000	1.203843	0.476281
C	0.000000	-1.203843	0.476281
C	0.000000	0.000000	-0.247790
H	0.000000	2.077216	2.461294
H	0.000000	-2.077216	2.461294
H	0.000000	2.134827	-0.078535
H	0.000000	-2.134827	-0.078535
C	0.000000	0.000000	-1.795805
O	0.000000	-1.159843	-2.333720
O	0.000000	1.159843	-2.333720
Ag	0.000000	0.000000	4.806383
Ag	0.000000	0.000000	7.433168

$[(Ag_7)^{-1}\text{-}Nin^-]^{-2}$

N	0.000000	0.000000	2.365190
C	0.000000	1.166043	1.667181
C	0.000000	-1.166043	1.667181
C	0.000000	1.203397	0.270689
C	0.000000	-1.203397	0.270689
C	0.000000	0.000000	-0.454268
H	0.000000	2.075583	2.257795
H	0.000000	-2.075583	2.257795
H	0.000000	2.135703	-0.282002
H	0.000000	-2.135703	-0.282002
C	0.000000	0.000000	-2.001941
O	0.000000	-1.159063	-2.543742
O	0.000000	1.159063	-2.543742
Ag	0.000000	0.000000	4.636469
Ag	0.000000	0.000000	7.284345
Ag	0.000000	0.000000	10.154355
Ag	0.000000	0.000000	12.823538
Ag	0.000000	0.000000	15.612318
Ag	0.000000	0.000000	18.358544
Ag	0.000000	0.000000	21.041449

$[(Ag_5)^{-1}\text{-}Nin^-]^{-2}$

N	0.000000	0.000000	2.451288
C	0.000000	1.164433	1.753048
C	0.000000	-1.164433	1.753048
C	0.000000	1.202970	0.355423
C	0.000000	-1.202970	0.355423
C	0.000000	0.000000	-0.370387
H	0.000000	2.073185	2.345330
H	0.000000	-2.073185	2.345330
H	0.000000	2.136178	-0.195822
H	0.000000	-2.136178	-0.195822
C	0.000000	0.000000	-1.917774
O	0.000000	-1.158344	-2.462811
O	0.000000	1.158344	-2.462811
Ag	0.000000	0.000000	4.771899
Ag	0.000000	0.000000	7.424492
Ag	0.000000	0.000000	10.312426
Ag	0.000000	0.000000	13.034650
Ag	0.000000	0.000000	15.762914

$[(Ag_3)^{-1}\text{-}Nin^{-}]^{-2}$

N	0.000000	0.000000	2.512697
C	0.000000	1.161644	1.813761
C	0.000000	-1.161644	1.813761
C	0.000000	1.202383	0.414217
C	0.000000	-1.202383	0.414217
C	0.000000	0.000000	-0.313048
H	0.000000	2.069139	2.409069
H	0.000000	-2.069139	2.409069
H	0.000000	2.136950	-0.135016
H	0.000000	-2.136950	-0.135016
C	0.000000	0.000000	-1.859857
O	0.000000	-1.157218	-2.410163
O	0.000000	1.157218	-2.410163
Ag	0.000000	0.000000	4.943546
Ag	0.000000	0.000000	7.629461
Ag	0.000000	0.000000	10.463306

wB97X-D/LanL2DZ Optimized geometries of $[(Ag_n)^q\text{-}Oin^-]^{q-1}$ systems

$[(Ag_3)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.548556
C	0.000000	1.158198	1.848755
C	0.000000	-1.158198	1.848755
C	0.000000	1.207871	0.447754
C	0.000000	-1.207871	0.447754
C	0.000000	0.000000	-0.266040
H	0.000000	2.068577	2.438073
H	0.000000	-2.068577	2.438073
H	0.000000	2.150401	-0.085557
H	0.000000	-2.150401	-0.085557
C	0.000000	0.000000	-1.764914
O	0.000000	-1.130888	-2.394871
O	0.000000	1.130888	-2.394871
Ag	0.000000	0.000000	-4.458529
Ag	0.000000	0.000000	-7.296833
Ag	0.000000	0.000000	-9.910703

$[(Ag_5)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.616802
C	0.000000	1.158144	1.916836
C	0.000000	-1.158144	1.916836
C	0.000000	1.207763	0.515833
C	0.000000	-1.207763	0.515833
C	0.000000	0.000000	-0.198135
H	0.000000	2.068596	2.506100
H	0.000000	-2.068596	2.506100
H	0.000000	2.150164	-0.017741
H	0.000000	-2.150164	-0.017741
C	0.000000	0.000000	-1.697473
O	0.000000	-1.130950	-2.326705
O	0.000000	1.130950	-2.326705
Ag	0.000000	0.000000	-4.394472
Ag	0.000000	0.000000	-7.222084
Ag	0.000000	0.000000	-9.854335
Ag	0.000000	0.000000	-12.680776
Ag	0.000000	0.000000	-15.298328

$[(Ag_7)^{+1}\text{-}Oin^-]^0$

N	0.000000	0.000000	2.710677
C	0.000000	1.158120	2.010622
C	0.000000	-1.158120	2.010622
C	0.000000	1.207709	0.609622
C	0.000000	-1.207709	0.609622
C	0.000000	0.000000	-0.104438
H	0.000000	2.068605	2.599860
H	0.000000	-2.068605	2.599860
H	0.000000	2.150049	0.075929
H	0.000000	-2.150049	0.075929
C	0.000000	0.000000	-1.603983
O	0.000000	-1.130978	-2.232893
O	0.000000	1.130978	-2.232893
Ag	0.000000	0.000000	-4.302556
Ag	0.000000	0.000000	-7.125672
Ag	0.000000	0.000000	-9.761670
Ag	0.000000	0.000000	-12.575136
Ag	0.000000	0.000000	-15.211489
Ag	0.000000	0.000000	-18.037080
Ag	0.000000	0.000000	-20.655087

$[(Ag_2)^0\text{-}Oin^-]^{-1}$

N	0.000000	0.000000	2.551713
C	0.000000	1.156647	1.846180
C	0.000000	-1.156647	1.846180
C	0.000000	1.204487	0.445239
C	0.000000	-1.204487	0.445239
C	0.000000	0.000000	-0.275160
H	0.000000	2.069248	2.434161
H	0.000000	-2.069248	2.434161
H	0.000000	2.142820	-0.096484
H	0.000000	-2.142820	-0.096484
C	0.000000	0.000000	-1.791001
O	0.000000	-1.136976	-2.392661
O	0.000000	1.136976	-2.392661
Ag	0.000000	0.000000	-4.615775
Ag	0.000000	0.000000	-7.282805

$[(Ag_7)^{-1}\text{-}Oin^-]^{-2}$

N	0.000000	0.000000	2.783620
C	0.000000	1.156548	2.077446
C	0.000000	-1.156548	2.077446
C	0.000000	1.204340	0.676551
C	0.000000	-1.204340	0.676551
C	0.000000	0.000000	-0.044223
H	0.000000	2.069453	2.665147
H	0.000000	-2.069453	2.665147
H	0.000000	2.142250	0.133975
H	0.000000	-2.142250	0.133975
C	0.000000	0.000000	-1.561187
O	0.000000	-1.137563	-2.160768
O	0.000000	1.137563	-2.160768
Ag	0.000000	0.000000	-4.394869
Ag	0.000000	0.000000	-7.079665
Ag	0.000000	0.000000	-9.940128
Ag	0.000000	0.000000	-12.609490
Ag	0.000000	0.000000	-15.434377
Ag	0.000000	0.000000	-18.169160
Ag	0.000000	0.000000	-20.875380

$[(Ag_5)^{-1}\text{-}Oin^-]^{-2}$

N	0.000000	0.000000	2.711355
C	0.000000	1.156281	2.003883
C	0.000000	-1.156281	2.003883
C	0.000000	1.203663	0.602974
C	0.000000	-1.203663	0.602974
C	0.000000	0.000000	-0.119508
H	0.000000	2.069688	2.591401
H	0.000000	-2.069688	2.591401
H	0.000000	2.140386	0.057963
H	0.000000	-2.140386	0.057963
C	0.000000	0.000000	-1.642341
O	0.000000	-1.141501	-2.230670
O	0.000000	1.141501	-2.230670
Ag	0.000000	0.000000	-4.550530
Ag	0.000000	0.000000	-7.231417
Ag	0.000000	0.000000	-10.190112
Ag	0.000000	0.000000	-12.903633
Ag	0.000000	0.000000	-15.665073

$[(Ag_3)^{-1}\text{-}Oin^-]^{-2}$

N	0.000000	0.000000	2.641578
C	0.000000	1.155999	1.932182
C	0.000000	-1.155999	1.932182
C	0.000000	1.202686	0.531254
C	0.000000	-1.202686	0.531254
C	0.000000	0.000000	-0.194034
H	0.000000	2.070169	2.519524
H	0.000000	-2.070169	2.519524
H	0.000000	2.137505	-0.017739
H	0.000000	-2.137505	-0.017739
C	0.000000	0.000000	-1.727658
O	0.000000	-1.148275	-2.296929
O	0.000000	1.148275	-2.296929
Ag	0.000000	0.000000	-4.789893
Ag	0.000000	0.000000	-7.493424
Ag	0.000000	0.000000	-10.413307