Electronic Supplementary Information for Dalton Transactions

How are PX_4^+, $P_2X_5^+$ and $AsBr_4^+$ Formed? Why didn't we Succeed to Prepare AsI_4^+? A Theoretical Study.

by

M. Gonsior, I. Krossing*

[a)] M.Sc. Marcin Gonsior, Universität Karlsruhe, Institut für Anorganische Chemie, Engesserstr. Geb. 30.45, 76128 Karlsruhe, e-mail: gonsior@chemie.uni-karlsruhe.de

[b)] Prof. Ingo Krossing, Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Inorganic and Coordination Chemistry (LCIC), ISIC-BCH, 1015 Lausanne, Switzerland, e-mail: ingo.krossing@epfl.ch

Computed Total Energies of all Species

Tab. A. Total energy, zero point energy, solvation energy and thermal and entropic contributions at 298K to the free energy of all calculated species in [H] (at MP2/TZVPP level).

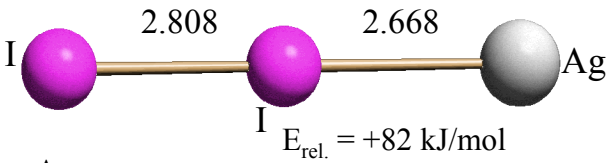
Molecule (symmetry)	*U (MP2/TZVPP)*	*ZPE (MP2/TZVPP)*	*H_{solv}(BP86/SVP) COSMO*	*Thermal+Entropic correc. to G at 298K*
$AsBr_2^+$ (C_{2v})	–7379.34087	0.00197	–0.08149	–0.02874
AsI_2^+ (C_{2v})	–2256.84173	0.00158	–0.07563	–0.03070
PBr_2^+ (C_{2v})	–5485.74848	0.00264	–0.07953	–0.02701
PI_2^+ (C_{2v})	–363.24680	0.00221	–0.07384	–0.02902
$AsBr_4^+$ (T_d)	–12524.56758	0.00444	–0.06447	–0.03171
AsI_4^+ (T_d)	–2279.56412	0.00335	–0.06262	–0.03606
PBr_4^+ (T_d)	–10630.99836	0.00574	–0.06472	–0.02926
PI_4^+ (T_d)	–385.98251	0.00444	–0.06119	–0.03382
$As_2Br_5^+$ (C_s)	–17331.67684	0.00608	–0.06210	–0.04104
$As_2I_5^+$ (C_s)	–4525.41879	0.00490	–0.05905	–0.04589
$P_2Br_5^+$ (C_s)	–13544.51217	0.00830	–0.06013	–0.03617
$P_2I_5^+$ (C_s)	–738.24532	0.00686	–0.05709	–0.04130
$AsBr_3$ (C_{3v})	–9952.28126	0.00283	–0.00353	–0.03156
AsI_3 (C_{3v})	–2268.50920	0.00223	–0.00407	–0.03460
PBr_3 (C_{3v})	–8058.68874	0.00368	–0.00188	–0.02972
PI_3 (C_{3v})	–374.91413	0.00301	–0.00281	–0.03386
Br_2 ($D_{\infty h}$)	–5145.14283	0.00076	–0.00165	–0.02236
I_2 ($D_{\infty h}$)	–22.65132	0.00054	–0.00256	–0.02593
AgBr ($C_{\infty v}$)	–2719.12161	0.00056	–0.01338	–0.02495
AgI ($C_{\infty v}$)	–157.86742	0.00047	–0.01270	–0.02580
$Ag(CH_2Cl_2)_3^+$ (C_2)	–3022.16690	0.08808	–0.06004	0.02628
CH_2Cl_2 (C_{2v})	–958.61384	0.02794	–0.00404	0.00621
$Ag(Br_2AsBr)_2^+$ (C_2)	–20050.87880	0.00658	–0.06035	–0.05379
$Ag(I_2AsI)_2^+$ (C_2)	–4683.35030	0.00534	–0.05675	–0.05920
$Ag(Br_2PBr)_2^+$ (C_2)	–16263.68695	0.00826	–0.05923	–0.04980
$Ag(I_2PI)_2^+$ (C_2)	–896.15586	0.00687	–0.05600	–0.05573
$(CH_2Cl_2)Ag(Br_2AsBr)^+$ (C_s)	–11057.20394	0.03400	–0.06268	–0.02085
$(CH_2Cl_2)Ag(I_2AsI)^+$ (C_s)	–3373.44045	0.03331	–0.06083	–0.02479
$(CH_2Cl_2)Ag(Br_2PBr)^+$ (C_s)	–9163.60810	0.03483	–0.06253	–0.01915
$(CH_2Cl_2)Ag(I_2PI)^+$ (C_s)	–1479.84299	0.03413	–0.06059	–0.02212

$(BrAsBr_2)Ag(Br_2)^+$ (C_1)	–15243.72475	0.00459	–0.06369	–0.04852
$(IAsI_2)Ag(I_2)^+$ (C_1)	–2437.47006	0.00370	–0.06081	–0.05215
$(BrPBr_2)Ag(Br_2)^+$ (C_1)	–13350.12867	0.00541	–0.06336	–0.04685
$(IPI_2)Ag(I_2)^+$ (C_1)	–543.88327	0.00446	–0.06041	–0.05054
$(I_3As)Ag(AsI_3)^+$ (C_{2h})	–4683.34179	0.00598	–0.05619	–0.05699
$(Br_3As)Ag(AsBr)_3^+$ (C_{2h})	–20050.86558	0.00751	–0.06058	–0.04902
$(I_3P)Ag(PI_3)^+$ (C_{2h})	–896.16867	0.00790	–0.05611	–0.05262
$(Br_3P)Ag(PBr_3)^+$ (C_{2h})	–16263.70295	0.00966	–0.05817	–0.04505
$(I_3As)Ag(I_2AsI)^+$ (C_1)	–4683.34815	0.00568	–0.05777	–0.05803
$(Br_3As)Ag(Br_2AsBr)^+$ (C_1)	–20050.87359	0.00700	–0.06177	–0.05290
$(I_3P)Ag(I_2PI)^+$ (C_1)	–896.16348	0.00741	–0.05705	–0.05431
$(Br_3P)Ag(Br_2PBr)^+$ (C_1)	–16263.69562	0.00884	–0.05925	–0.05276
$(I_3As)Ag(CH_2Cl_2)^+$ (C_1)	–3373.43618	0.03372	–0.06345	–0.02289
$(Br_3As)Ag(CH_2Cl_2)^+$ (C_1)	–11057.19895	0.03451	–0.06526	–0.01915
$(I_3P)Ag(CH_2Cl_2)^+$ (C_1)	–1479.84946	0.03467	–0.06213	–0.02088
$(Br_3P)Ag(CH_2Cl_2)^+$ (C_1)	–9163.61733	0.03559	–0.06294	–0.01704
(I_3As) $(I_2)Ag^+$ (C_s)	–2437.46516	0.00400	–0.06000	–0.05083
$(Br_3P)(Br_2)Ag^+$ (C_s)	–13350.14656	0.00652	–0.06281	–0.04429
$(I_3P)(I_2)Ag^+$ (C_s)	–543.88068	0.00504	–0.05968	–0.04873
$(Br_3As)(Br_2)Ag^+$ (C_s)	–15243.71845	0.00521	–0.06060	–0.04544
$(I_3P)Ag(I_2)^+$ (C_1)	–543.88960	0.00501	–0.06103	–0.04924
$(Br_3P)Ag(Br_2)^+$ (C_1)	–13350.13710	0.00621	–0.06321	–0.04340
$(I_3As)Ag(I_2)^+$ (C_1)	–2437.47608	0.00403	–0.06136	–0.05142
$(Br_3As)Ag(Br_2)^+$ (C_1)	–15243.71831	0.00513	–0.06538	–0.04544
$(P_4)Ag(Br_2AsBr)^+$ (C_s)	–11462.22182	0.01039	–0.05967	–0.04401
$Ag(P_4)_2^+$ (D_{2h})	–2873.56265	0.01403	–0.05940	–0.03253
$Ag(I_2)_2^+$ (C_{2h})	–191.60812	0.00254	–0.06588	–0.04342
$Ag(Br_2)_2^+$ (C_{2h})	–10436.56854	0.00254	–0.06890	–0.04342

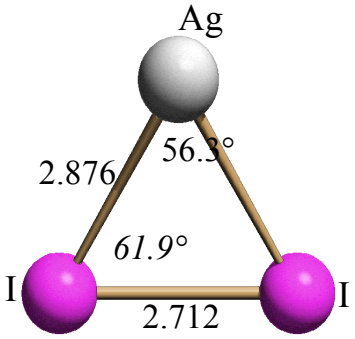
$Ag(X_2)^+$ Energies and structures (X = Br, I; MP2/TZVPP)

	U	ZPE	H(0K)	E(rel) (kJ/mol)
plan.90grad AgBr2+	-5291.39275	0.001189	-5291.39156	0
plan.90grad AgI2+	-168.912853	0.0009276	-168.911925	0
cycle AgBr2+	-5291.39143	0.0010611	-5291.39036	+3.13
cycle AgI2+	-168.912452	0.000854	-168.911598	+0.86
*** linear AgBr2+**	-5291.36826	0.0009651	-5291.36729	+63.71
*** linear AgI2+**	-168.881567	0.0007277	-168.880839	+81.62
* 2 imaginary Frequencies				

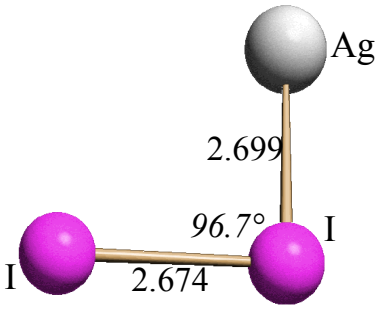
Optimized $Ag(X_2)^+$ structures at the MP2/TZVPP level (X = Br, I):



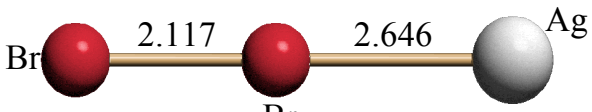
$E_{rel.}$ = +82 kJ/mol
N(imag) = 2



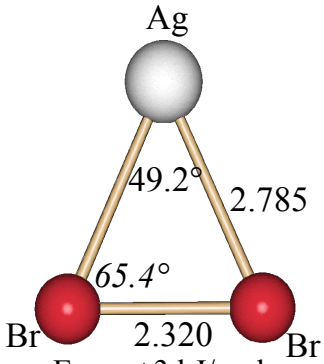
$E_{rel.}$ = +1 kJ/mol
N(imag) = 0



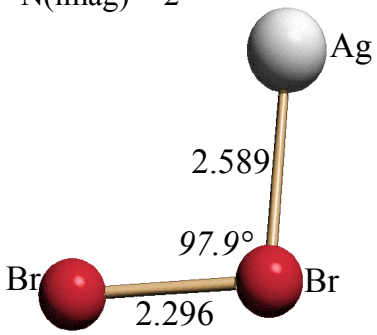
$E_{rel.}$ = 0 kJ/mol
N(imag) = 0



$E_{rel.}$ = +64 kJ/mol
N(imag) = 2



$E_{rel.}$ = +3 kJ/mol
N(imag) = 0



$E_{rel.}$ = +0 kJ/mol
N(imag) = 0

Deposited Born Haber Cycles and Auxiliary Data

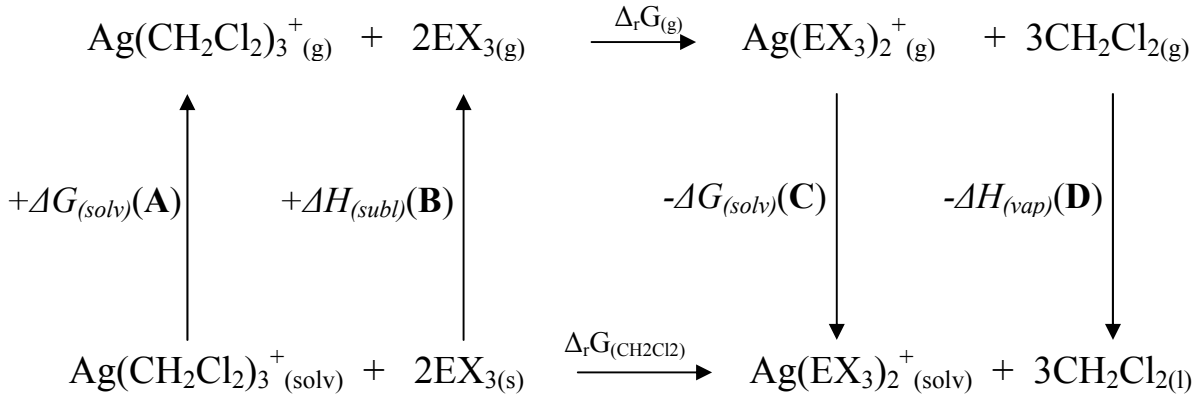


Fig. A. The Born-Haber cycle for the formation of the $Ag(EX_3)_2^+$ complexes in solution for E = As, P and X = Br, I. The general formula $Ag(EX_3)_2^+$ denotes here the most favorable isomer: $(I_3P)Ag(PI_3)^+$, $(BrPBr_2)Ag(PBr_3)^+$ and for E = As and X = Br, I it is the $(XEX_2)Ag(X_2EX)^+$ isomer.

Tab. B. The enthalpies in the Born-Haber cycle (in $kJ \cdot mol^{-1}$) of the formation of complexes $Ag(EX_3)_2^+$ in the reaction $Ag(CH_2Cl_2)_3^+ + 2EX_3 \rightarrow Ag(EX_3)_2^+ + 3CH_2Cl_2$ (*X = Br, I; E = As, P*). The letters A-D denotes ΔG or ΔH for the processes of sublimation, solvation or evaporation in the Fig. A.

E, X	**A**	**B**	**C**	**D**	$\Delta_r G_{(g)}$	$\Delta G^{298K}_{(CH_2Cl_2)}$
As, Br	+158	+84	–158	–87	–26	–29
As, I	+158	+119	–149	–87	–64	–23
P, Br	+158	+78	–155	–87	–35	–41
P, I	+158	+88	–147/–150 [b)]	–87	–70/–63[b)]	–58/–53[a)]

[a)] values calculated for the $(I_3P)Ag(I_2PI)^+$ isomer.

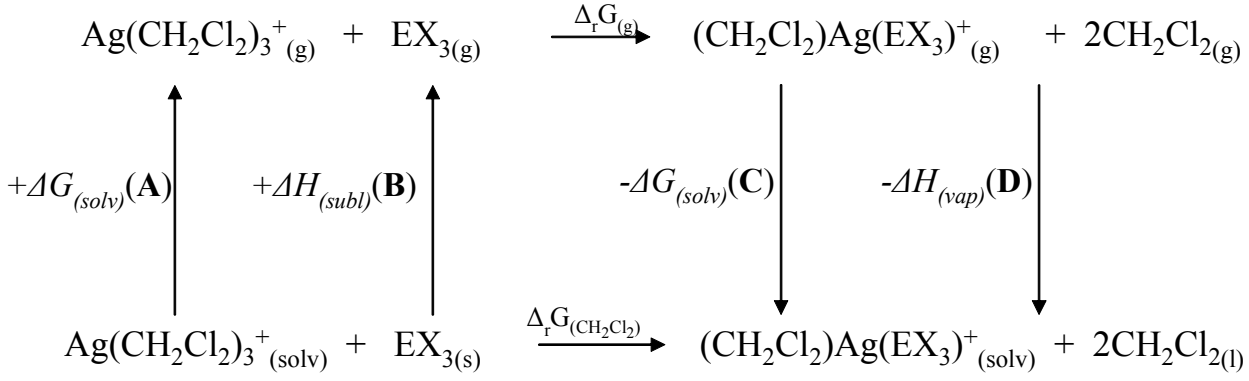


Fig. B. The Born-Haber cycle for the formation in solution of the following complexes: $(CH_2Cl_2)Ag(X_2EX)^+$ for E = As; X = Br, I) and $(CH_2Cl_2)Ag(EX_3)^+$ (for E = P; X = Br, I). The general formula $Ag(EX_3)_2^+$ denotes here the most favorable isomer and does not express the appropriate geometry.

Tab. C. The enthalpies in the Born-Haber cycle (in $kJ \cdot mol^{-1}$) of the formation of complexes $(CH_2Cl_2)Ag(EX_3)^+$ in the reaction $Ag(CH_2Cl_2)_3^+ + EX_3 \rightarrow (CH_2Cl_2)Ag(EX_3)^+ + 2CH_2Cl_2$ (*X = Br, I; E = As, P*). The letters A-D denotes ΔG or ΔH for the processes of sublimation, solvation or evaporation in the Fig. B.

E, X	**A**	**B**	**C**	**D**	$\Delta_rG_{(g)}$	$\Delta G^{298K}_{(CH_2Cl_2)}$
As, Br	+158	+42	–165	–58	+3	–20
As, I	+158	+59	–160	–58	–22	–23
P, Br	+158	+39	–165	–58	–6	–32
P, I	+158	+44	–163	–58	–23	–42

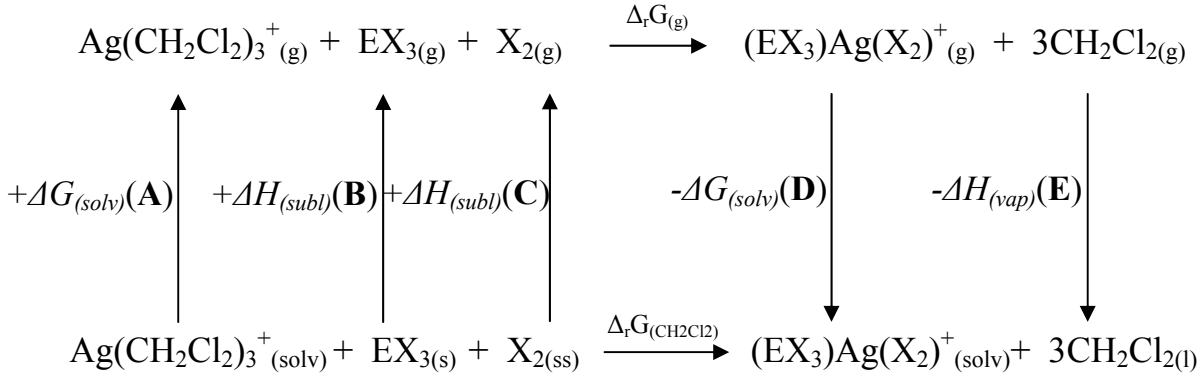


Fig. C. The Born-Haber cycle for the formation of the $(EX_3)Ag(X_2)^+$ complexes in solution for E = As, P and X = Br, I. The general complex formula $(EX_3)Ag(X_2)^+$ denotes different types of coordination. For every complex the most favorable geometry was taken.

Tab. D. The enthalpies for the formation of the most favorable complexes of type $(EX_3)Ag(X_2)^+$ in the reaction $Ag(CH_2Cl_2)_3^+ + EX_3 + X_2 \rightarrow (EX_3)Ag(X_2)^+ + 3CH_2Cl_2$ (*X = Br, I; E = As, P*) in the Born-Haber cycle (in $kJ \cdot mol^{-1}$). The letters A-D denotes ΔG or ΔH for the processes of sublimation, solvation or evaporation in the Fig. C.

Type of $(EX_3)Ag(X_2)^+$ isomer formed	**A**	**B**	**C**	**D**	**E**	**$\Delta_r G_{(g)}$**	**$\Delta G^{298K}_{(CH_2Cl_2)}$**
$(BrAsBr_2)Ag(Br)_2^+$	+158	+42	+31	–167	–87	+6	–17
$(I_3As)Ag(I_2)^+$	+158	+59	+63	–161	–87	–22	+10
$(Br_3P)(Br_2)Ag^+$	+158	+39	+31	–165	–87	–22	–46
$(I_3P)Ag(I_2)^+$	+158	+44	+63	–160	–87	–41	–23