Weakly Coordinating Anions

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Coordination Chemistry of Diiodine and Implications for the Oxidation Capacity of the Synergistic Ag^+/X_2 ($X=$ Cl, Br, I) System

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Abstract: *The synergistic Ag^+/X_2 system ($X=Cl$, Br, I) is a very strong, but ill-defined oxidant—more powerful than X_2 or Ag^+ alone. Intermediates for its action may include $[Ag_m(X_2)_n]^{m+}$ complexes. Here, we report on an unexpectedly variable coordination chemistry of diiodine towards this direction: (**A**)Ag-I_2-Ag(**A**), $[Ag_2(I_2)_4]^{2+}(\mathbf{A}^-)_2$ and $[Ag_2(I_2)_6]^{2+}(\mathbf{A}^-)_2\cdot(I_2)_{x\approx0.65}$ form by reaction of Ag(**A**) (**A** $=Al(OR^F)_4$; $R^F=C(CF_3)_3$) with diiodine (single crystal/powder XRD, Raman spectra and quantum-mechanical calculations). The molecular (**A**)Ag-I_2-Ag(**A**) is ideally set up to act as a 2 e^- oxidant with stoichiometric formation of 2 AgI and 2 $\mathbf{A}^-$. Preliminary reactivity tests proved this (**A**)Ag-I_2-Ag(**A**) starting material to oxidize n-C_5H_{12}, C_3H_8, CH_2Cl_2, P_4 or S_8 at room temperature. A rough estimate of its electron affinity places it amongst very strong oxidizers like MF_6 ($M=4d$ metals). This suggests that (**A**)Ag-I_2-Ag(**A**) will serve as an easily in bulk accessible, well-defined, and very potent oxidant with multiple applications.*

During the quest for strong, but readily available oxidants, hundreds of systems were investigated—from elemental fluorine, through high-valent metal fluorides, to highly oxidizing organics such as "Magic Blue".[1] Among those, the synergistic Ag^+/X_2 system ($X=$ Cl, Br, I) proved to be a powerful oxidant—much stronger than Ag^+ or X_2 alone—and oxidizes polyhalogenated triarylamines to the corresponding radical cations, the true oxidants in the famous Magic Blue, that is, tris(4-bromophenyl)aminium hexachloroantimonate. This route enabled, for example, the oxidation of C_{60} to $C_{60}^{+\bullet}$ by the hexabromophenylcarbazole radical cation.[2] The latter has a redox potential of +1.36 V (vs. Fc/Fc^+ in CH_2Cl_2; cf. Ag/Ag^+ in CH_2Cl_2: +0.65 V[1]), but record redox potentials of up to +1.72 V (vs. Fc/Fc^+ in CH_2Cl_2) were reported for $N(C_6Cl_5)_3^{+\bullet}$ in situ generated from $Ag^+/Cl_2/N(C_6Cl_5)_3$.[1]

However, what is the origin of this increased Ag^+/X_2 oxidation potential? Due to the low pK_s values of AgX ($K_s=$ equilibrium solubility constant of AgX), the residual aqueous X^- concentration is minimal in the presence of silver ions. Therefore, the redox potential of the pair 0.5 X_2/X^- is shifted in aqueous solution in the presence of Ag^+ ions at standard conditions by $\Delta E^0_X=+0.059\ \text{V}\,pK_{s,AgX}$. This leads to the very high combined system potentials $E^0_{X_2/Ag^+/AgX}$ of +1.49 V (iodine, $\Delta E^0_I=+0.95$ V), +1.82 V (bromine, $\Delta E^0_{Br}=+0.73$ V), and even +1.93 V (chlorine, $\Delta E^0_{Cl}=+0.57$ V), exceeding the thermodynamic water stability window. Changing from coordinating water/ammonia to less polar and weakly coordinating solvents, causes drastic further absolute electrochemical potential shifts of Ag^+/Ag^0: Thus, if going from water/ammonia to 1,2-$Cl_2C_2H_4$, $\Delta E_{abs}{}^0$ increases by +0.67/+1.71 V.[3] Therefore, even higher ΔE^0 shifts can be expected for the synergistic Ag^+/X_2 systems in suitable low polarity solvents with low AgX solubility/high pK_s(AgX) values. Although the Ag^+/X_2 system is a very strong, but accessible and affordable oxidant, its action remains ill-defined. Any investigation of the mechanism, how this oxidizing Ag^+/X_2 mixture actually works, is hitherto missing. Of course, chemical intuition suggests that there is a coordination of X_2 to Ag^+, leading to a polarization of the X_2 molecule with formation of AgX and, formally, a highly reactive "X^+". Yet, the latter should act as a strong X^+-donor and makes this assumption questionable. Alternatively one would have to postulate a $[Ag\text{-}X\text{-}X\text{-}Ag]^{2+}$ moiety, able to accept two e^-. However, examples for observed X_2-complexes to prove this assumption are scarce: one example assigned in matrix studies as $AuF_5\cdot F_2$,[4] and only three metal-I_2 complexes isolated at room temperature are known: polymeric $Ag(I_2)MF_6$ ($M=$ As, Sb)[5] and $[Rh_2(O_2CCF_3)_4(I_2)]\cdot I_2$.[6]

Recently, we reported[7] the ion pairs $Ag(X_2)\mathbf{A}$ ($X=$ Cl, Br, I) as the first Cl_2 or Br_2 complexes. Owing to the poor binding energy of the dihalogen bases and the expected high reactivity, we used $[Al(OR^F)_4]^-$ ($R^F=C(CF_3)_3$; $\mathbf{A}^-$) as counterion.[8] It stabilizes weakly bound complexes like $[Ag(P_4)_2]^+$,[9] $[Ag(C_2H_2)_4]^+$[10] or $[Ag(Fe(CO)_5)_2]^+$,[11] and is also compatible with strong electrophiles and oxidants like $[CCl_3]^+$,[12] $[P_9]^+$,[13] or $[NO_2]^+$.[14] Using our new,[7] facile route to donor-free Ag**A** (**1**),[15] we now prepared (**A**)Ag-I_2-Ag(**A**) (**2**), $[Ag_2(I_2)_4]^{2+}(\mathbf{A}^-)_2$ (**3**) and $[Ag_2(I_2)_6]^{2+}(\mathbf{A}^-)_2\cdot(I_2)_{x\approx0.65}$ (**4**), and investigated the capacity of molecular (**A**)Ag-I_2-Ag(**A**) (**2**) to serve as an oxidant.

With C_6F_{14} as a solvent, the synthesis and crystallization of the double ion pair (**A**)Ag-I_2-Ag(**A**) (**2**) and the salt $[Ag_2$-

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Supporting information for this article, containing synthetic procedures, behavior of **2**, **3**, and **4** in SO_2, a note on the existence of $Ag(I_2)_4{}^+$, thermodynamics of $\mathbf{3}^{2+}$ in the crystal, Raman spectra of the obtained Ag^+-I_2 complexes together with assignment of the bands, NMR spectra of the product of reaction between **2** and C_5H_{12} in C_6F_{14}, crystal structures details, and computational data, can be found under:
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$(I_2)_4]^{2+}(\mathbf{A}^-)_2$ (**3**) was possible, whereas $[Ag_2(I_2)_6]^{2+}(\mathbf{A}^-)_2\cdot(I_2)_x$ ($x\approx 0.65$–0.82) (**4**) formed neat or in SO_2 solution (Figure 1, the charged compound number abbreviates the bare cation, that is, $\mathbf{4}^{2+}$ stands for $[Ag_2(I_2)_6]^{2+}$). The Ag^+-I_2 complexes can also be handled in SO_2 at room temperature, but we observed precipitation of neat I_2 in cold SO_2 (−28 °C), which has an increased dielectric constant ($\varepsilon_r = 13.6$ at 25 °C vs. 19 at −28 °C[16]). This suggests that the solution stability is finely balanced and at the edge of what may be realized (compare the Supporting Information).

The crystal structure of **2** in Figure 1 is derived from the ion pair **1** by double addition to the iodine atoms in I_2 and retention of the intramolecular Ag**A** bonding pattern.[28] It is a molecular ion pair with no intermolecular contacts below 3 Å and hence it is soluble in C_6F_{14}. **3** and **4** are true salts with no significant secondary Ag−O or Ag−F contacts, except for one long Ag−F and I−F contact in **3** (Figure 1). The I_2 molecules in **2**–**4** are bound either terminal (t-I_2) to one Ag^+, or they bridge two silver cations (b-I_2). The main structural features of **2**–**4** are L-shaped Ag-I-I units with bond angles between 89° and 103°, and with $d_{\text{Ag-I}}$ being larger than $d_{\text{I-I}}$ (d = distance). Apart from the b-I_2 unit in $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$, $d_{\text{I-I}}$ is almost unchanged to gaseous I_2. This unexpected feature was already observed in $Ag(X_2)\mathbf{A}$,[7] $Ag(I_2)MF_6$[5] and $[Rh_2(O_2CCF_3)_4(I_2)]\cdot I_2$.[6] It was also computed for the related bridged H^+-X_2-H^+ systems (X = Cl, Br).[17]

The terminal I–I distances in **3**–**4** are rather similar to that in free $I_{2(g)}$. Although the values directly listed by the SHELXL program are slightly shorter, libration may play a role. Correcting for this (see section 5b in the Supporting Information), does not systematically alter the distances. In **2**, $d_{\text{Ag-I}}$ is shorter than in solid AgI (2.81 Å), indicating rather intimate Ag-X interactions. In **3** and **4**—the I_2-rich compounds—an I⋯I halogen bond occurs between t-I_2 (donor) and b-I_2 (acceptor) molecules. This interaction led to an elongation of the b-I_2 bond. Similarly, the free I_2 molecules in the voids of **4** also interacted with t-I_2 from $\mathbf{4}^{2+}$. Only two structural precedents to I⋯I halogen bonding were reported,[18] namely in $I_5[SbF_6]$ and $[Rh_2(O_2CCF_3)_4(I_2)]\cdot I_2$ (but not mentioned as a donor–acceptor halogen bond[6,19]). In addition, halogen bonding between two I_2 molecules was DFT calculated.[20] Similar arrangements were observed in recent polybromide networks.[21]

In agreement with $d(t\text{-}I_2)$ being similar to $I_{2(g)}$, the Raman spectra of **2**–**4** all contain ν(I-I) bands at 208 to 210 cm^{-1}, and thus near the values for gaseous I_2 (215 cm^{-1}, see Figure 1 and section 3 in the Supporting Information for a full assignment). The terminal ν(I-I) values are near the relative I_5^+ (207 cm^{-1})[5] as well as $Ag(I_2)SbF_6$ (208 cm^{-1}).[5] **3** and **4** contain very intense, slightly red-shifted $\nu(b\text{-}I_2)$ bands at 190 cm^{-1}, when b-I_2 is engaged in a halogen bond to t-I_2, and at 196 cm^{-1}, if the b-I_2 molecule does not interact with t-I_2 in **3**.

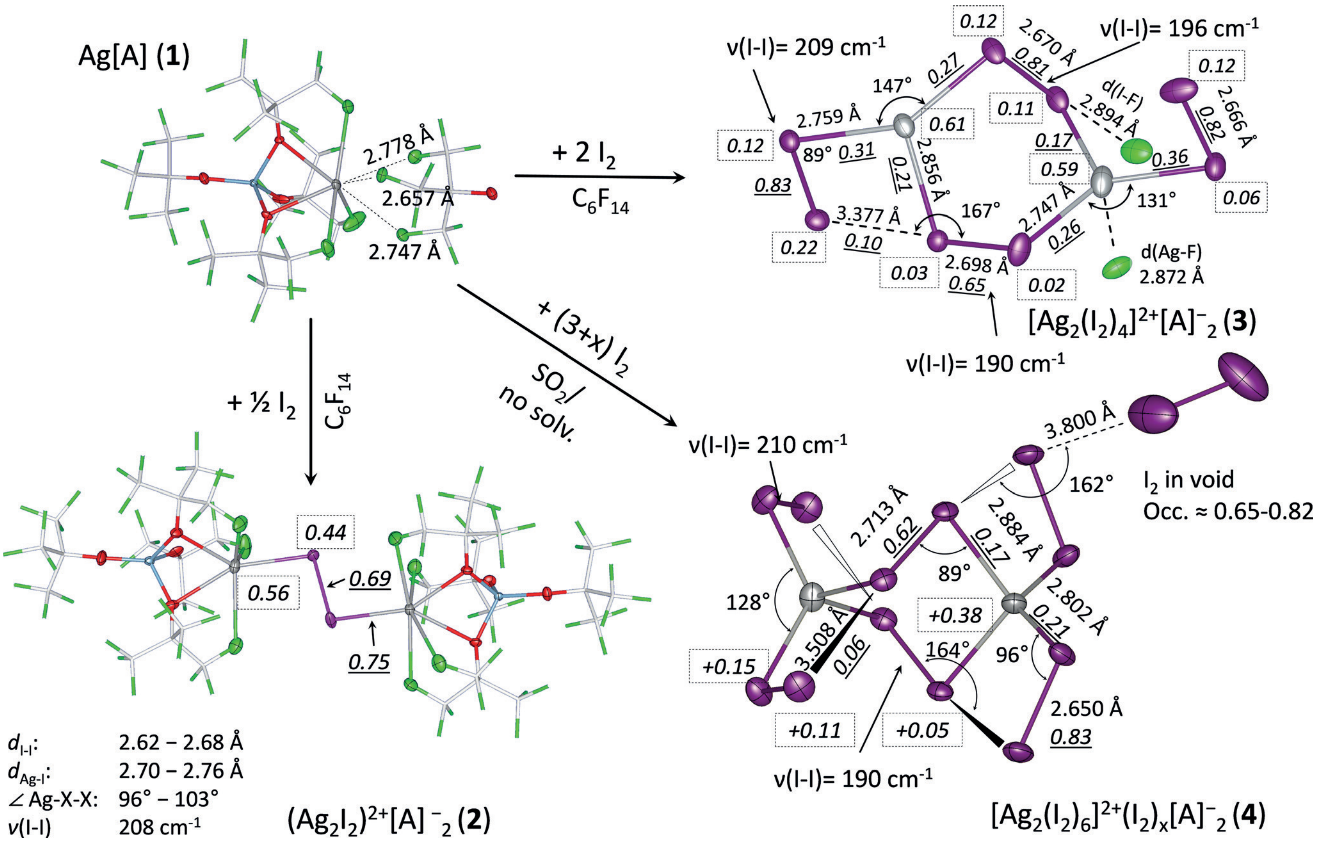

Figure 1. Schematic presentation of the reactions between **1** and diiodine together with sections of the molecular structures of the starting silver salt (taken from Ref. [7]) and compounds **2**–**4**. The most important bond lengths (Å) and angles (°) are listed together with the observed Raman bands of predominant I–I nature, ν(I–I) [cm^{-1}], as well as DFT-calculated partial charges (PABOON, in dashed boxes) and shared electron numbers (SEN; PABOON analysis at B3-LYP/D3/def2-TZVPP level). Intermolecular Ag−F contacts are drawn as dotted line. Color scheme: Al: blue, O: red, Ag: gray, C: white, F: light green, I: violet.

The vibrational modes, $\nu(t\text{-I}_2)$ in particular, could be well assigned with the help of DFT (compare section 6c in the Supporting Information), with $\nu(b\text{-I}_2)$ being underestimated by about 10 to 20 cm^{-1}. More importantly, the 6 cm^{-1} difference in $\nu(b\text{-I}_2)$ for the two different b-I$_2$ molecules in $\mathbf{3}^{2+}$ is reproduced well. In agreement with our earlier work,[7] the I$_2$ unit donates with both, the bonding π- and antibonding π*-MO to the Ag$^+$ acceptor. Overall this (almost) cancels the structural effect on bond lengths and stretching frequency. However, if compared to solid I$_2$ (2.715 Å[22]/181 and 190 cm^{-1}), all terminal $d_{\text{I-I}}/\nu(t\text{-I}_2)$ values in **2**–**4** are shorter/blue-shifted.

The most polarizable donor I$_2$ forms a relatively strong bond to silver ($\Delta_r H^0 = -135$ kJ mol^{-1}), and also the subsequent uptake of I$_2$ up to [Ag(I$_2$)$_4$]$^+$ is favored in the gas phase by 61 to 117 kJ mol^{-1}. However, the Coulomb repulsion in the gaseous dications $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, and $\mathbf{4}^{2+}$—calculated from Coulomb's law to be larger than +200 kJ mol^{-1} for +1 point charges on Ag atoms—makes the dimerization unfavorable. Thus, gaseous $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ are unstable towards dissociation to the singly charged ions Ag$^+$ + Ag(I$_2$)$^+$, 2 Ag(I$_2$)$_2{}^+$ and 2 Ag(I$_2$)$_3{}^+$ by about 150–200 kJ mol^{-1} in $\Delta_r G^0$. In the crystal, they owe their existence to the lattice energy gain of the [A$_2$]$^{2+}$([B]$^-$)$_2$ salts, if compared to two competing A$^+$B$^-$ salts. This gain was estimated to amount to more than 300 kJ mol^{-1} on the basis of the Jenkins equation.[23] It was exemplarily worked out for lattice stabilized (Ag$_2$(I$_2$)$_6$)[A]$_2$ in comparison to two [Ag(I$_2$)$_3$](**A**) (Figure 2 bottom; for more details see the Supporting Information).

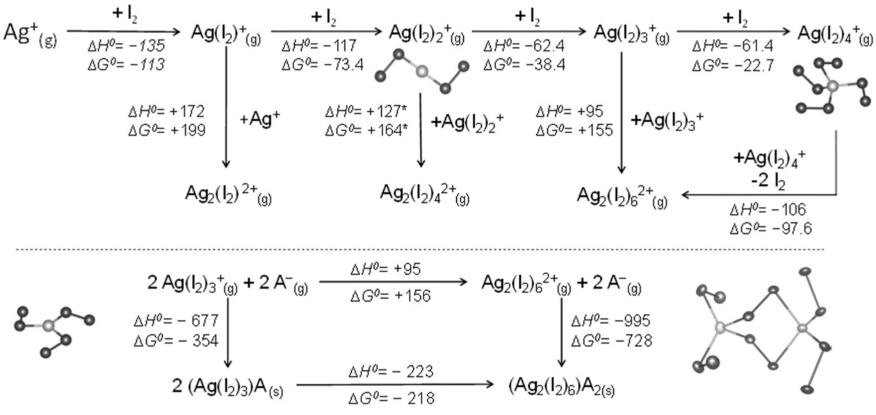

Figure 2. Top: Schematic presentation of the thermodynamics of formation of various Ag$^+$-I$_2$ complexes in the gas phase (ΔG^0, ΔH^0) in kJ mol^{-1}. Bottom: BFHC cycle for estimation of lattice energy gain in the dication salt [Ag$_2$(I$_2$)$_6$]$^{2+}$(A$^-$)$_2$ as compared to the hypothetical monocation salt [Ag(I$_2$)$_3$]$^+$(A$^-$). For clarity, the hypothetic [Ag(I$_2$)$_3$]$^+$ and experimental [Ag$_2$(I$_2$)$_6$]$^{2+}$ structures are shown. The reference value for the formation of Ag(I$_2$)$^+$ derives from a CCSD(T)/(CBS) calculation (italics), the others were calculated at the B3-LYP/D3/def2-TZVPP level, which for the smaller systems gave results very close to CCSD(T)/(CBS) (cf. Ref. [7]).

Compound **2** includes the prospect to function as a potent and "clean" oxidant[3,7] easily accessible in bulk quantities. Upon accepting two electrons, the following reaction (1) should occur [Eq. (1)],

$$(\text{Ag}_2\text{I}_2)[\mathbf{A}]_2 + 2\,\text{e}^- \rightarrow 2\,\text{AgI}\downarrow + 2\,\mathbf{A}^- \qquad (1)$$

leaving only solid AgI and **A**$^-$ as the counterion for the cation formed. The large lattice energy of AgI and its insolubility in C$_6$F$_{14}$ greatly increases the oxidation potential of I$_2$ in the presence of Ag$^+$. Therefore, we have performed preliminary reactivity tests of **2** dissolved in C$_6$F$_{14}$. Upon addition of relatively unreactive substrates like the aliphatic alkanes C$_5$H$_{12}$ or C$_3$H$_8$, the violet solution decolorized within minutes and, visibly as well as by powder XRD, the formation of yellowish AgI was evident. Also CH$_2$Cl$_2$, o-C$_6$H$_4$F$_2$, P$_4$ and S$_8$ proved to react with **2**. By contrast, the more stable gases Xe, SO$_2$, C$_2$H$_6$ and CH$_4$ appeared to be unreactive. Ordering the results of the reactions according to the ionization potential (IP) of the substrates (Figure 3), suggests that the oxidizing power of **2** appears to be sufficient for molecules with an IP of up to about 11.4 eV.

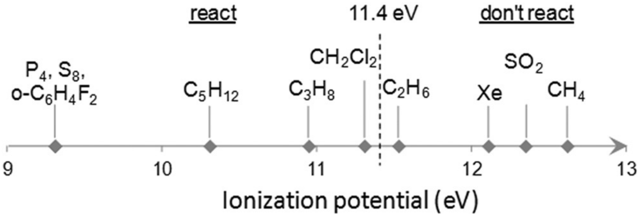

Figure 3. Schematic representation of the compounds reactivity towards **2** in C$_6$F$_{14}$ ordered according to the ionization potentials of the substrates.

Due to the preliminary nature, we have conducted only basic investigations of some of the products using NMR spectroscopy in C$_6$F$_{14}$ and SO$_2$ as solvents (compare Figure S9 in the Supporting Information). We have found C$_5$H$_{12}$ to give products that show ^{13}C NMR singlets in the very low field region (ca. +250 ppm). Analysis of the spectra allows concluding that the formed species is a carbocation, but no indication for CI$_3{}^+$ ($\delta^{13}\text{C} = 97$),[24] or other C-I species that due to the inverse halogen dependence of the chemical shift of the I atom[25] should appear rather high-field shifted, was observed. A decomposition of the **A**$^-$ anion was detected for the reaction with propane and pentane, which could be a result of the high reactivity and Brønsted acidity of the carbocations formed. Reaction with P$_4$ yielded initially a species with P$_5{}^+$ cage, but the main final product was the P$_9{}^+$ cation.[13] It has to be stressed that apparently iodine bonds to the oxidized substrates are only formed in very small amounts, underlining the importance of Equation (1) as being the relevant for oxidation chemistry. A detailed description of the mechanism and products of the reactions was beyond the scope of the studies, and the issue will be addressed in a follow up paper. In any

Table 1: Experimental or calculated electron affinity values of X_2, **2** and MF_6 for comparison.

Reaction	−EA [eV]	Source or calculational level
1) $^1/_2\,X_2(g) + e^-(g) \rightarrow X^-(g)$		
1a) $X = Cl$	2.42/ 1.15	(exp.)[a]/B3LYP-D3/SV(P)[b]
1b) $X = Br$	2.27/ 1.61	(exp.)/B3LYP-D3/SV(P)[b]
1c) $X = I$	2.02/ 2.35	(exp.)/B3LYP-D3/SV(P)[b]
2) $^1/_2\,[Ag_2I_2(A)_2](g) + e^-(g) \rightarrow I^-(g) + Ag^+(g) + [A]^-(g)$	4.15	B3LYP-D3/SV(P)[b]
3) $^1/_2\,[Ag_2I_2(A)_2](g) + e^-(g) \rightarrow I^-(g) + Ag[A]$(g, ion pair)	9.93	B3LYP-D3/SV(P)[b]
4) $^1/_2\,[Ag_2I_2(A)_2](g) + e^-(g) \rightarrow AgI(g) + [A]^-(g)$	11.31	B3LYP-D3/SV(P)[b] + exp. values AgI[c]
5) $^1/_2\,[Ag_2I_2(A)_2](g) + e^-(g) \rightarrow AgI(solid) + [A]^-(g)$	13.36	B3LYP-D3/SV(P)[b] + exp. values AgI[d]
For comparison: $[MF_6](g) + e^-(g) \rightarrow [MF_6]^-(g)$		
6) M = Mo	4.23	(Dixon/Christe, adiabatic value)[26]
7) M = Tc	5.89	(Dixon/Christe, adiabatic value)[26]
8) M = Ru	7.01	(Dixon/Christe, adiabatic value)[26]
9) M = Rh	6.80	(Dixon/Christe, adiabatic value)[26]
10) M = Pd	7.95	(Dixon/Christe, adiabatic value)[26]
11) M = Pt	7.0/8.0	(exp.)[27a]/(exp.)[27b]

[a] $\Delta H° = \Delta_f H°(X, 298.15\ K) + vEA(X) + R \cdot 298.15\ K$; $\Delta_f H°(X, 298.15\ K)$ taken from CRC Handbook of Chemistry and Physics;[16] vEA(X) was taken from the NIST Chemistry Webbook at http://webbook.nist.gov/chemistry/. [b] All B3LYP-D3/SV(P) calculations were performed without zero-point energy corrections, as **2** proved too large for a computational evaluation of the vibrational spectrum. Entry 3 contains the standard gas-phase complexation enthalpy of $Ag^+(g) + \mathbf{A}^-(g) \rightarrow Ag\mathbf{A}(g)$ calculated at the same level (−558 kJ mol^{-1} or 5.78 eV). [c] This value was obtained by adding the experimental $\Delta_{latt}H°(AgI)$ (−9.21 eV) to entry 2 and subtracting the experimental $\Delta_{subl}H°(AgI)$ (+2.05 eV) thereof. [d] This value was obtained by adding the experimental $\Delta_{latt}H°(AgI)$ (−9.21 eV) to entry 2. $\Delta_{subl}H°(AgI)$ and $\Delta_{latt}H°(AgI)$ were taken from the CRC Handbook of Chemistry and Physics.[16]

case, the preliminary results allow to state that **2** is indeed a powerful and potentially very useful oxidizer. A (due to different standard states and neglect of ZPE and thermal contributions) crude estimation for the enormous thermodynamic driving force of the formation of gaseous or solid AgI on the electron affinity (EA) of the complexed I_2 molecule in **2** can be gathered from Table 1: Thus, already the coordination of I_2 by two molecular Ag(**A**) entities increases the electron affinity of 0.5 I_2 giving I^- from −2.02 eV to −4.15 eV for gaseous **2** (entry 2, Table 1). Gas-phase formation of molecular Ag**A** or AgI in entry 3 and 4 (Table 1) further shifts the electron affinity of **2** to −9.93/−11.31 eV. Compared to the pure gas phase reaction, the lattice enthalpy (889 kJ mol^{-1}/9.21 eV) of AgI finally shifts the electron uptake reaction to −13.36 eV (entry 5, Table 1). However, we like to warn people to draw conclusions concerning redox potentials in condensed phases, as solvation and lattice effects are neglected, which may shift absolute values by some eV. Moreover, for size restrictions on the calculation of full **2** (118 heavy atoms), we had to stick to the simple (dispersion corrected) B3LYP-D3/SV(P) method. For an evaluation of the (reasonable) performance of this method see the Supporting Information. Some other gas-phase electron affinity reactions of the very potent gaseous oxidizers MF_6 (M = Mo, Tc, Ru, Rh, Pd) elaborated by Dixon and Christe at highest possible levels[26] or measured experimentally (M = Pt)[27] are shown for comparison as entries 6–11 in Table 1 and suggest that **2** stands in this line. In addition, the range of the assessed EAs in entries 2–5 in Table 1 match reasonably with the experimental findings described above in Figure 3.

In conclusion, we have shown that diiodine does have a considerable and unexpected coordination chemistry and even forms homoleptic, dicationic silver–diiodine complexes with up to six diiodine molecules. The preliminary reactivity tests on **2** proved it to be a potent oxidizer. It appears that direct Ag^+-X_2 interactions are the mechanistic reason for the greatly increased oxidation capabilities of the synergistic, but poorly understood Ag^+/X_2 system. The in multigram scale available and easily weighable bulk **2** in combination with a chemically robust solvent is expected to serve as a well-defined stoichiometric oxidant with interesting further applications in synthetic chemistry.

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[28] CCDC 1434974 – 1434976 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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