

Weakly Coordinating Anions

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Silver Complexes of Dihalogen Molecules

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Abstract: The perfluorohexane-soluble and donor-free silver compound $\text{Ag}(\mathbf{A})$ ($\mathbf{A} = \text{Al}(\text{OR}^F)_4$; $\text{R}^F = \text{C}(\text{CF}_3)_3$) prepared using a facile novel route has unprecedented capabilities to form unusual and weakly bound complexes. Here, we report on the three dihalogen–silver complexes $\text{Ag}(\text{Cl}_2)\mathbf{A}$, $\text{Ag}(\text{Br}_2)\mathbf{A}$, and $\text{Ag}(\text{I}_2)\mathbf{A}$ derived from the soluble silver compound $\text{Ag}(\mathbf{A})$ (characterized by single-crystal/powder XRD, Raman spectra, and quantum-mechanical calculations).

Examples of any stable Lewis acid (LA)– X_2 ($\text{X} = \text{halogen atom}$) complexes are scarce: the published data only include one example assigned in matrix studies as AuF_5F_2 ,^[1] and only three metal– I_2 complexes isolated at room temperature: polymeric $\text{Ag}(\text{I}_2)\text{MF}_6$ ($\text{M} = \text{As}, \text{Sb}$)^[2] and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{I}_2)]\cdot\text{I}_2$.^[3] In a very formal way, one may also address X^+ as the acceptor of a X_2 donor in $[\text{X}_3]^+$ (“ $[\text{X}^+](\text{X}_2)$ ”, $\text{X} = \text{Cl}$,^[4] Br ,^[5] I ^[6]) and $[\text{X}_5]^+$ (“ $[\text{X}^+](\text{X}_2)_2$ ”, $\text{X} = \text{Br}$,^[7] I ^[8]). Several related complexes of coinage metal halides with very weak bases like Xe were studied in the gas phase (see Ref. [9] and references therein). However, no reports of any Cl_2 or Br_2 complexes were hitherto published, probably due to the very poor basicity of X_2 with proton affinities comparable to CH_3Cl (647^[10] vs. 653 kJ mol^{−1} for I_2 ^[11]), C_2H_6 (596^[10] vs. 586 kJ mol^{−1} for Br_2 ^[12]) or CO_2 (541^[10] vs. 550 kJ mol^{−1} for Cl_2 ^[13]). Owing to the poor binding energy of the dihalogen bases in the targeted complexes and their expected high reactivity, we decided to use the perfluorinated alkoxyaluminate $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ ($\mathbf{A}^-$)—one of the best weakly coordinating anions (WCAs)—as counterion.^[14,15] It stabilizes weakly bound complexes like $[\text{Ag}(\text{P}_4)_2]^+$,^[16] $[\text{Ag}(\text{C}_2\text{H}_2)_4]^+$ ^[17] or $[\text{Ag}(\text{Fe}(\text{CO})_5)_2]^+$.^[18] But in addition, $\mathbf{A}^-$ is also compatible with strong electrophiles and oxidants like $[\text{CCl}_3]^+$,^[19] $[\text{P}_9]^+$,^[20] or $[\text{NO}_2]^+$.^[21] Quite uncommon for WCAs, it can be easily and safely obtained in multi-gram scale as Ag^+ salt $\text{Ag}\mathbf{A}$ ($\mathbf{1}$).^[22] Using a novel route to donor-free $\mathbf{1}$, we now prepared the three X_2 complexes $\text{Ag}(\text{X}_2)\mathbf{A}$ ($\text{X} = \text{Cl}$ ($\mathbf{2}$), Br ($\mathbf{3}$), I ($\mathbf{4}$)).

Although $\mathbf{1}$ is known since 15 years,^[23] the access to solvent-free $\mathbf{1}$ is tedious and includes prolonged heating at high vacuum conditions (10^{−6} mbar) to allow for synthesis of

truly “naked” $\mathbf{1}$. In the course of this project, we realized that, astonishingly, $\mathbf{1}$ is slightly soluble in perfluorinated solvents, like perfluorohexane C_6F_{14} or the perfluorinated morpholine derivative Fluorinert® (FC-770). These solvents have chemical resistance hard to surpass, and they guarantee the weakest coordination of Ag^+ achievable in solution. This solubility now enabled the facile and high yield synthesis of solvent-free $\mathbf{1}$ by the reaction of $\text{Li}\mathbf{A}$ with AgF in perfluorohexane, including its first crystallization and structural characterization. It turned out that $\text{Ag}\mathbf{A}$ is an ion pair, with the Ag^+ cation connected to the $\mathbf{A}^-$ anion by two weak intramolecular $\text{Ag}–\text{O}$ (2.496 Å and 2.503 Å), and three weak $\text{Ag}–\text{F}$ interactions (2.596 Å, 2.610 Å, 2.612 Å). In that respect, it resembles the known $\text{Ag}(\text{SO}_2)\mathbf{A}$ complex.^[24] What makes $\mathbf{1}$ special, are the three weak intermolecular $\text{Ag}–\text{F}$ contacts to the neighboring anion (see Figure 1), making the site ready to be substituted by any base, stronger than the rather distant and weakly coordinating $-\text{C}(\text{CF}_3)_3$ group. For this reason, it is both possible and necessary to use perfluorinated solvents to handle $\mathbf{1}$ with retention of its large Lewis acidity. Even SO_2 or CH_2Cl_2 coordinate too strongly to Ag^+ (see Table 1 and discussion). With C_6F_{14} as a solvent, the synthesis and crystallization of the ion pairs $\text{Ag}(\text{Cl}_2)\mathbf{A}$ ($\mathbf{2}$), $\text{Ag}(\text{Br}_2)\mathbf{A}$ ($\mathbf{3}$), and $\text{Ag}(\text{I}_2)\mathbf{A}$ ($\mathbf{4}$) was possible by addition of excess X_2 ($\text{X} = \text{Cl}, \text{Br}$) or a stoichiometric amount of I_2 to a suspension of $\mathbf{1}$ (Figure 1). Upon reaction, the suspensions cleared and the soluble complexes $\mathbf{2}–\mathbf{4}$ yielded single crystals suitable for X-ray analysis upon slow cooling of the solution.

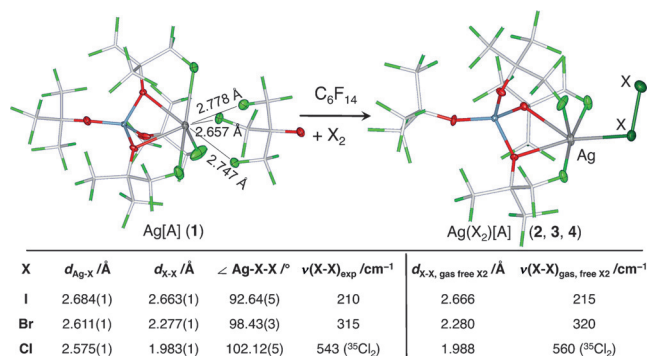


Figure 1. Reactions between $\mathbf{1}$ and the dihalogen molecules X_2 in perfluorohexane together with sections of the molecular structures of the starting silver salt and compounds $\mathbf{2}–\mathbf{4}$. The most important bond lengths (Å) and angles (°) are listed together with the observed Raman bands of predominant X_2 nature, $\nu(\text{X-X})_{\text{exp}}$, and for comparison the experimental values $d_{\text{X-X, gas, free X}_2}$ and $\nu(\text{X-X})_{\text{gas, free X}_2}$ for the free gaseous X_2 molecules. Intermolecular $\text{Ag}–\text{F}$ contacts in $\mathbf{1}$ to one $\text{OC}(\text{CF}_3)_3$ moiety in a neighboring molecule are drawn as dotted line. Color Scheme: Al: blue, O: red, Ag: gray, C: white, F: light green, halogen (Cl, Br or I) atom in $\text{Ag}(\text{X}_2)\mathbf{A}$: dark green.

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Table 1: Thermodynamics of the formation of various Ag^+-X_2 and $\text{Ag}^+-\text{solvent}$ complexes in the gas phase (ΔG° , ΔH°) in kJ mol^{-1} . The values given in bold are from the most reliable CCSD(T) calculations extrapolated to the complete basis set limit (CBS).

Reaction	DFT (def2-TZVPP/D3)						CCSD(T)/CBS	
	BP86		B3-LYP		PBE0		$\Delta_r H^\circ$	$\Delta_r G^\circ$
$\text{Ag}^+ + \text{Solvent}$	$\Delta_r H^\circ$	$\Delta_r G^\circ$	$\Delta_r H^\circ$	$\Delta_r G^\circ$	$\Delta_r H^\circ$	$\Delta_r G^\circ$	$\Delta_r H^\circ$	$\Delta_r G^\circ$
$\text{Ag}^+ + \text{SO}_2 \rightarrow \text{Ag}(\text{OSO})^+$	–	–	–	–	–109	–84	–102	–75
$\text{Ag}^+ + \text{CH}_2\text{Cl}_2 \rightarrow \text{Ag}(\text{CH}_2\text{Cl}_2)^+$	–	–	–	–	–136	–107	–137	–110
$\text{Ag}^+ + \text{HOC}(\text{CF}_3)_3 \rightarrow \text{Ag}(\text{F}_3\text{C})_3\text{COH}^+$	–90	–57	–83	–50	–76	–43	–	–
$\text{Ag}^+ + \text{Dihalogen } \text{X}_2$								
$\text{Ag}^+ + \text{F}_2 \rightarrow \text{AgF}_2^+$	–	–	–	–	–	–	–22	–3
$\text{Ag}^+ + \text{Cl}_2 \rightarrow \text{AgCl}_2^+$	–92	–68	–77	–53	–74	–49	–77	–55
$\text{Ag}^+ + \text{Br}_2 \rightarrow \text{AgBr}_2^+$	–121	–98	–103	–79	–100	–76	–101	–80
$\text{Ag}^+ + \text{I}_2 \rightarrow \text{AgI}_2^+$	–163	–139	–139	–115	–136	–112	–135	–113
$\text{AgA} + \text{Dihalogen } \text{X}_2$								
	DFT (B3-LYP/SV(P)/D3)							
			$\Delta_r H^\circ$	$\Delta_r G^\circ$				
$\text{AgA}_{(\text{g})} + \text{Cl}_{2,(\text{g})} \rightarrow \text{Ag}(\text{Cl}_2)\text{A}_{(\text{g})}$	–	–	–34	+0.4	–	–	–	–
$\text{AgA}_{(\text{g})} + \text{Br}_{2,(\text{g})} \rightarrow \text{Ag}(\text{Br}_2)\text{A}_{(\text{g})}$	–	–	–45	–11	–	–	–	–
$\text{AgA}_{(\text{g})} + \text{I}_{2,(\text{g})} \rightarrow \text{Ag}(\text{I}_2)\text{A}_{(\text{g})}$	–	–	–63	–28	–	–	–	–

The crystal structures of **2–4** in Figure 1 show that these compounds derive from **1** by simple substitution of the coordinating $-\text{C}(\text{CF}_3)_3$ group with one X_2 molecule and retention of the intramolecular $\text{Ag}-\text{A}$ bonding pattern.^[31] Alike **1**, they are molecular ion pairs with no intermolecular contacts below 3 Å and hence, they are soluble in C_6F_{14} . The X_2 molecules in **2–4** are terminally bound to one Ag atom. The main structural features of **2–4** are L-shaped $\text{Ag}-\text{X}-\text{X}$ units with bond angles between 93° and 102°, and with distance $d_{\text{Ag}-\text{X}}$ being larger than $d_{\text{X}-\text{X}}$.

The distance $d_{\text{X}-\text{X}}$ in **2–4** is within 3–5 times the standard deviation, unchanged to gaseous X_2 . There may be an effect of libration, correcting for this (see Section 3b in the Supporting Information), gives the bond lengths in the range 1.983–2.052 (**2**), 2.277–2.324 (**3**) and 2.665–2.773 Å (**4**), but the most probable 2/1-corrected values are again indistinguishable from those in gaseous X_2 . Similar observations were made for $\text{Ag}(\text{I}_2)\text{MF}_6$ ^[2] and $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{I}_2)] \cdot \text{I}_2$.^[3] It was also computed for the related H^+-X_2 ($\text{X} = \text{Cl}, \text{Br}$).^[25] In **2–4**, $d_{\text{Ag}-\text{X}}$ is 0.13 to 0.28 Å shorter than in the corresponding silver halides (AgCl : 2.773 Å, AgBr : 2.887 Å, AgI : 2.81 Å), indicating rather intimate $\text{Ag}-\text{X}$ interactions.

In agreement with $d_{\text{X}-\text{X}}$ being similar to $\text{X}_{2(\text{g})}$, the Raman spectra of **2–4** all contain bands with predominant $\nu(\text{X}-\text{X})$ character near the values for gaseous X_2 molecules (see Figure 1 for the $\nu(\text{X}-\text{X})$ bands). The terminal $\nu(\text{X}-\text{X})$ stretches are among the highest ever recorded and suggest decoupling of the $\nu(\text{X}-\text{X})$ mode from admixtures of bands including the silver atom. They are similar to Cl_3^+ (515 cm^{-1}),^[26] Br_5^+ (309 cm^{-1})^[5] and I_5^+ (207 cm^{-1})^[2] as well as $\text{Ag}(\text{I}_2)\text{SbF}_6$ (208 cm^{-1}).^[2]

The relatively low Ag^+-X_2 binding Gibbs energies and enthalpies in comparison to the competing solvent complexes and $\text{Ag}(\text{F}_3\text{C})_3\text{COH}^+$ formation as a model for the intermolecular aggregation of solid **1** given in Table 1, give a hint why hitherto complexes with Br_2 or Cl_2 remained unknown.

Clearly, the most polarizable donor I_2 forms the strongest bond to silver ($\Delta_r H^\circ$ 135 kJ mol^{-1}). Its strength is comparable to the $\text{Ag}^+-\text{CH}_2\text{Cl}_2$ complex (cf. the difficulty to remove CH_2Cl_2 from solid **1** prepared in CH_2Cl_2 ^[23]). Br_2 binds significantly weaker ($\Delta_r H^\circ$ 101 kJ mol^{-1}), and similar to a SO_2 molecule. As expected, Cl_2 forms the weakest bond, similar in strength to the calculated $\text{Ag}^+-\text{CF}_3\text{COH}$ model interaction. This suggests that the weakness of the interaction of the coordinated Cl_2 molecule is close to the thermodynamic limit of **1** to form stable complexes. To test the influence of the coordinated A^- anion on the energetics of the Ag^+-X_2 complexes, calculations of the entire $\text{Ag}(\text{X}_2)\text{A}$ ion pairs were done, although at lower quality due to size restrictions

(see the Supporting Information; $\text{X} = \text{Cl}-\text{I}$; B3-LYP/SV(P)/D3). They show that the X_2 dissociation energies decrease by about 43 to 87 kJ mol^{-1} , if compared to that of the isolated gaseous $\text{Ag}(\text{X}_2)^+$ cation (B3-LYP/D3 values). Overall, the calculations suggest that $\text{Ag}(\text{X}_2)\text{A}$ is at the limit of stability. The fact that **2** can only be handled at lower temperatures and in an atmosphere of Cl_2 agrees with the calculated $\Delta_r G^\circ$ of +0.4 kJ mol^{-1} for the reaction.

As judged from first principles, it would be rather intuitive to assume that the Ag^+-X_2 bond is formed by a donation of the antibonding $\pi^*(\text{X}_2)$ HOMO to the Ag^+ acceptor. However, that would cause a shortening of $d_{\text{X}-\text{X}}$ and a blue shift of $\nu(\text{X}-\text{X})$, like observed in $[\text{I}_2]^+$,^[27] where an electron is removed from the π^* -HOMO. This is contrary to our observations, and thus there must also be a contribution of a $\pi(\text{X}_2) \rightarrow \text{Ag}^+$ donation, as also stated for $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{I}_2] \cdot \text{I}_2$.^[11] Indeed our calculations show that the vicinity of the orbital energies $\pi(\text{X}_2)$ at $-8.7/-9.9/-11.0$ eV and $\pi^*(\text{X}_2)$ at $-7.1/-7.8/-8.4$ eV ($\text{I}_2/\text{Br}_2/\text{Cl}_2$) allows both to donate to the Ag^+ acceptor (-10.6 eV; all orbital energies at B3-LYP/def2-TZVPP/D3); the graphic visualization of the orbitals shows this as well (see the Supporting Information). Overall the $\text{X}-\text{X}$ -contracting ($\pi^*(\text{X}_2)$ -donation) and $\text{X}-\text{X}$ -elongating ($\pi(\text{X}_2)$ -donation) contributions almost cancel, leaving rather unchanged $\text{X}-\text{X}$ distances and stretching frequencies. This conclusion is confirmed by the results of the population analyses (AIM,^[28] NPA^[29] or PABOON^[30]) collected in Table 2.

Especially the comparison of the electron densities residing on the bond critical point of free X_2 and AgX_2^+ shows that despite of the silver coordination, the $\text{X}-\text{X}$ bond is virtually unchanged. The significant covalency of the Ag^+-X_2 interaction is supported by the calculated $\rho(\text{BCP})$ values, the Wiberg bond index WBI and the shared electron number SEN that all suggest increasing $\text{Ag}-\text{X}$ covalency, if going from $\text{X} = \text{Cl}$ to I .

Table 2: Results of the population analyses AIM, NPA and PABOON calculated with B3-LYP/def2-TZVPP/D3 on the bonding of X_2 and AgX_2^+ : dimensionless partial charges, calculated electron density residing on the bond critical point $\rho(\text{BCP})$ [$e \text{ \AA}^{-3}$], Wiberg Bond Index WBI and Shared Electron Number SEN.

Cation	Calculated Partial Charges at $Ag-X-X^{[a]}$			$\rho(\text{BCP})^{[b]}$		WBI/SEN	
	Paboon	NPA	AIM	X-X	M-X	X-X	M-X
$AgCl_2^+$	0.61/0.31/0.08	0.91/−0.02/0.11	0.84/0.04/0.12	1.026	0.346	1.030/0.849	0.184/0.645
$AgBr_2^+$	0.54/0.37/0.09	0.87/0.00/0.13	0.77/0.09/0.14	0.690	0.351	1.011/0.809	0.257/0.746
AgI_2^+	0.45/0.44/0.11	0.80/0.05/0.15	0.67/0.17/0.17	0.504	0.367	1.006/0.768	0.389/0.795

[a] Values rounded to 2 digits. Addition to non-unity may result from rounding errors. [b] For comparison, $\rho(\text{BCP})$ of free X_2 : 1.031 (Cl), 0.697 (Br), 0.509 (I) [$e \text{ \AA}^{-3}$].

In conclusion we have shown that the easily accessible, Lewis acidic silver ion pair **1** soluble in perfluorocarbons (!), allows to obtain Ag^+-X_2 complexes that significantly broadened the known set of compounds containing neutral X_2 molecules as Lewis bases. The $Ag-X_2$ complexes **2–4** show only slightly perturbed terminal d_{X-X} and ν_{X-X} values, if compared to gaseous X_2 . This is likely due to donation from the antibonding $\pi^*(X_2)$ as well as the bonding $\pi(X_2)$ molecular orbitals of the X_2 donor molecule. Perfluorinated hydrocarbon solvents are a necessary choice for synthesis of **2–4**, and may be very useful to handle further very weakly bound complexes deriving from **1**. In addition, it is probable that other (e.g. organic) transformations may be induced/catalyzed by the perfluorocarbon soluble **1**.

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