Weakly Coordinating Anions

International Edition: DOI: 10.1002/anie.201603741
German Edition: DOI: 10.1002/ange.201603741

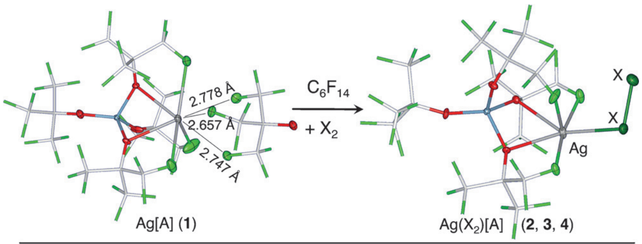
Silver Complexes of Dihalogen Molecules

*Przemysław J. Malinowski, Daniel Himmel, and Ingo Krossing**

Abstract: *The perfluorohexane-soluble and donor-free silver compound Ag(**A**) (**A** = Al(OR^F)$_4$; R^F = C(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 Ag(Cl$_2$)**A**, Ag(Br$_2$)**A**, and Ag(I$_2$)**A** derived from the soluble silver compound Ag(**A**) (characterized by single-crystal/powder XRD, Raman spectra, and quantum-mechanical calculations).*

Examples of any stable Lewis acid (LA)–X_2 (X = halogen atom) complexes are scarce: the published data only include one example assigned in matrix studies as AuF$_5$·F$_2$,[1] and only three metal–I$_2$ complexes isolated at room temperature: polymeric Ag(I$_2$)MF$_6$ (M = As, Sb)[2] and [Rh$_2$(O$_2$CCF$_3$)$_4$-(I$_2$)]·I$_2$.[3] In a very formal way, one may also address X^+ as the acceptor of a X_2 donor in [X_3]$^+$ ("[X^+](X_2)", X = Cl,[4] Br,[5] I[6]) and [X_5]$^+$ ("[X^+](X_2)$_2$", X = 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$_3$Cl (647[10] vs. 653 kJ mol^{-1} for I$_2$[11]), C$_2$H$_6$ (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 [Al(OC(CF$_3$)$_3$)$_4$]$^-$ (**A**$^-$)—one of the best weakly coordinating anions (WCAs)—as counterion.[14,15] It stabilizes weakly bound complexes like [Ag(P$_4$)$_2$]$^+$,[16] [Ag(C$_2$H$_2$)$_4$]$^+$[17] or [Ag(Fe(CO)$_5$)$_2$]$^+$.[18] But in addition, **A**$^-$ is also compatible with strong electrophiles and oxidants like [CCl$_3$]$^+$,[19] [P$_9$]$^+$,[20] or [NO$_2$]$^+$.[21] Quite uncommon for WCAs, it can be easily and safely obtained in multi-gram scale as Ag$^+$ salt Ag**A** (**1**).[22] Using a novel route to donor-free **1**, we now prepared the three X_2 complexes Ag(X_2)**A** (X = Cl (**2**), Br (**3**), I (**4**)).

Although **1** is known since 15 years,[23] the access to solvent-free **1** is tedious and includes prolonged heating at high vacuum conditions (10^{-6} mbar) to allow for synthesis of truly "naked" **1**. In the course of this project, we realized that, astonishingly, **1** is slightly soluble in perfluorinated solvents, like perfluorohexane C$_6$F$_{14}$ 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 **1** by the reaction of Li**A** with AgF in perfluorohexane, including its first crystallization and structural characterization. It turned out that Ag**A** is an ion pair, with the Ag$^+$ cation connected to the **A**$^-$ anion by two weak intramolecular Ag–O (2.496 Å and 2.503 Å), and three weak Ag–F interactions (2.596 Å, 2.610 Å, 2.612 Å). In that respect, it resembles the known Ag(SO$_2$)**A** complex.[24] What makes **1** special, are the three weak intermolecular Ag–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 –C(CF$_3$)$_3$ group. For this reason, it is both possible and necessary to use perfluorinated solvents to handle **1** with retention of its large Lewis acidity. Even SO$_2$ or CH$_2$Cl$_2$ coordinate too strongly to Ag$^+$ (see Table 1 and discussion). With C$_6$F$_{14}$ as a solvent, the synthesis and crystallization of the ion pairs Ag(Cl$_2$)**A** (**2**), Ag(Br$_2$)**A** (**3**), and Ag(I$_2$)**A** (**4**) was possible by addition of excess X_2 (X = Cl, Br) or a stoichiometric amount of I$_2$ to a suspension of **1** (Figure 1). Upon reaction, the suspensions cleared and the soluble complexes **2**–**4** yielded single crystals suitable for X-ray analysis upon slow cooling of the solution.



X	$d_{Ag\text{-}X}$ /Å	$d_{X\text{-}X}$ /Å	∠ Ag-X-X /°	ν(X-X)$_{exp}$ /cm^{-1}	$d_{X\text{-}X,\ gas\ free\ X2}$ /Å	ν(X-X)$_{gas,\ free\ X2}$ /cm^{-1}
I	2.684(1)	2.663(1)	92.64(5)	210	2.666	215
Br	2.611(1)	2.277(1)	98.43(3)	315	2.280	320
Cl	2.575(1)	1.983(1)	102.12(5)	543 (^{35}Cl$_2$)	1.988	560 (^{35}Cl$_2$)

Figure 1. Reactions between **1** and the dihalogen molecules X_2 in perfluorohexane together with sections of the molecular structures of the starting silver salt and compounds **2**–**4**. The most important bond lengths (Å) and angles (°) are listed together with the observed Raman bands of predominant X_2 nature, $\nu(X–X)_{exp}$, and for comparison the experimental values $d_{X\text{-}X,gas,free\ X2}$ and $\nu(X\text{-}X)_{gas,free\ X2}$ for the free gaseous X_2 molecules. Intermolecular Ag–F contacts in **1** to one OC(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 Ag(X_2)**A**: dark green.

---

[*] Dr. P. J. Malinowski, Dr. D. Himmel, Prof. Dr. I. Krossing
Institut für Anorganische und Analytische Chemie and
Freiburger Materialforschungszentrum (FMF)
Albert-Ludwigs-Universität Freiburg
Freiburg i. Br. (Germany)
E-mail: krossing@uni-freiburg.de

Dr. P. J. Malinowski
Centre of New Technologies, University of Warsaw
Warsaw (Poland)

Supporting information for this article, containing details to experimental and theoretical methods and references, can be found under:
http://dx.doi.org/10.1002/anie.201603741.

Table 1: Thermodynamics of the formation of various Ag^+–X_2 and Ag^+–solvent complexes in the gas phase (ΔG^0, ΔH^0) 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).

	DFT (def2-TZVPP/D3)						CCSD(T)/CBS	
Reaction	BP86		B3-LYP		PBE0			
$Ag^+ + $Solvent	$\Delta_rH°$	$\Delta_rG°$	$\Delta_rH°$	$\Delta_rG°$	$\Delta_rH°$	$\Delta_rG°$	**$\Delta_rH°$**	**$\Delta_rG°$**
$Ag^+ + SO_2 \rightarrow Ag(OSO)^+$	–	–	–	–	−109	−84	**−102**	**−75**
$Ag^+ + CH_2Cl_2 \rightarrow Ag(CH_2Cl_2)^+$	–	–	–	–	−136	−107	**−137**	**−110**
$Ag^+ + HOC(CF_3)_3 \rightarrow Ag(F_3C)_3COH^+$	−90	−57	−83	−50	−76	−43	–	–
$Ag^+ + $Dihalogen X_2								
$Ag^+ + F_2 \rightarrow AgF_2^+$	–	–	–	–	–	–	**−22**	**−3**
$Ag^+ + Cl_2 \rightarrow AgCl_2^+$	−92	−68	−77	−53	−74	−49	**−77**	**−55**
$Ag^+ + Br_2 \rightarrow AgBr_2^+$	−121	−98	−103	−79	−100	−76	**−101**	**−80**
$Ag^+ + I_2 \rightarrow AgI_2^+$	−163	−139	−139	−115	−136	−112	**−135**	**−113**
Ag**A** + Dihalogen X_2	DFT (B3-LYP/SV(P)/D3)							
			$\Delta_rH°$	$\Delta_rG°$				
$Ag\mathbf{A}_{(g)} + Cl_{2,(g)} \rightarrow Ag(Cl_2)\mathbf{A}_{(g)}$	–	–	−34	+0.4	–	–	–	–
$Ag\mathbf{A}_{(g)} + Br_{2,(g)} \rightarrow Ag(Br_2)\mathbf{A}_{(g)}$	–	–	−45	−11	–	–	–	–
$Ag\mathbf{A}_{(g)} + I_{2,(g)} \rightarrow Ag(I_2)\mathbf{A}_{(g)}$	–	–	−63	−28	–	–	–	–

The crystal structures of **2**–**4** in Figure 1 show that these compounds derive from **1** by simple substitution of the coordinating -$C(CF_3)_3$ group with one X_2 molecule and retention of the intramolecular Ag-**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 Ag–X–X units with bond angles between 93° and 102°, and with distance $d_{\text{Ag-X}}$ being larger than $d_{\text{X-X}}$.

The distance $d_{\text{X-X}}$ 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 $Ag(I_2)MF_6$[2] and $[Rh_2(O_2CCF_3)_4(I_2)]\cdot I_2$.[3] It was also computed for the related H^+-X_2 ($X = $ Cl, Br).[25] In **2**–**4**, $d_{\text{Ag-X}}$ 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 Ag-X interactions.

In agreement with $d_{\text{X-X}}$ being similar to $X_{2(g)}$, the Raman spectra of **2**–**4** all contain bands with predominant $\nu(X\text{-}X)$ character near the values for gaseous X_2 molecules (see Figure 1 for the $\nu(X\text{-}X)$ bands). The terminal $\nu(X\text{-}X)$ stretches are among the highest ever recorded and suggest decoupling of the $\nu(X\text{-}X)$ 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 $Ag(I_2)SbF_6$ (208 cm^{-1}).[2]

The relatively low Ag^+-X_2 binding Gibbs energies and enthalpies in comparison to the competing solvent complexes and $Ag(F_3C)_3COH^+$ 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 (Δ_rH^0 135 $kJ\,mol^{-1}$). Its strength is comparable to the Ag^+–CH_2Cl_2 complex (cf. the difficulty to remove CH_2Cl_2 from solid **1** prepared in CH_2Cl_2[23]). Br_2 binds significantly weaker (Δ_rH^0 101 $kJ\,mol^{-1}$), and similar to a SO_2 molecule. As expected, Cl_2 forms the weakest bond, similar in strength to the calculated Ag^+-$(CF_3)_3COH$ 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 $\mathbf{A}^-$ anion on the energetics of the Ag^+-X_2 complexes, calculations of the entire $Ag(X_2)\mathbf{A}$ ion pairs were done, although at lower quality due to size restrictions (see the Supporting Information; $X = $ Cl-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 $Ag(X_2)^+$ cation (B3-LYP/D3 values). Overall, the calculations suggest that $Ag(X_2)\mathbf{A}$ 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 $\Delta_rG°$ 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 $\pi^*(X_2)$ HOMO to the Ag^+ acceptor. However, that would cause a shortening of $d_{\text{X-X}}$ and a blue shift of $\nu(X\text{-}X)$, like observed in $[I_2]^+$,[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 $\pi(X_2) \rightarrow Ag^+$ donation, as also stated for $[Rh_2(O_2CCF_3)_4I_2]\cdot I_2$.[11] Indeed our calculations show that the vicinity of the orbital energies $\pi(X_2)$ at −8.7/−9.9/−11.0 eV and $\pi^*(X_2)$ at −7.1/−7.8/−8.4 eV ($I_2/Br_2/Cl_2$) 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 X–X-contracting ($\pi^*(X_2)$-donation) and X–X-elongating ($\pi(X_2)$-donation) contributions almost cancel, leaving rather unchanged X–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 X–X bond is virtually unchanged. The significant covalency of the Ag^+–X_2 interaction is supported by the calculated ρ(BCP) values, the Wiberg bond index WBI and the shared electron number SEN that all suggest increasing Ag–X covalency, if going from $X = $ 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 ρ(BCP) [e Å^{-3}], Wiberg Bond Index WBI and Shared Electron Number SEN.

	Calculated Partial Charges at Ag-*X*-*X*[a]			ρ(BCP)[b]		WBI/SEN	
Cation	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, ρ(BCP) of free X_2: 1.031 (Cl), 0.697 (Br), 0.509 (I) [e Å^{-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 $d_{X\text{-}X}$ and $\nu_{X\text{-}X}$ 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**.

Acknowledgements

The authors wish to thank the ERC for award of an Advanced Grant (UniChem) as well as the DFG in the Normalverfahren that financed part of the work. P.J.M. likes to thank the Polish Ministry of Science and Higher Education for financial support within Mobility Plus programme (grant number 895/MOB/2012/0). High-resolution Raman measurements were carried out by using the CePT infrastructure financed by the EU European Regional Development Fund within the Operational Programme “Innovative economy” for 2007–2013 (grant number POIG.02.02.00-14-024/08-00).

Keywords: crystal structures · density functional calculations · halogen molecules · Raman spectroscopy · weakly coordinating anions

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9259–9261
Angew. Chem. **2016**, *128*, 9405–9407

---

[1] D. Himmel, S. Riedel, *Inorg. Chem.* **2007**, *46*, 5338–5342.
[2] T. S. Cameron, J. Passmore, X. Wang, *Angew. Chem. Int. Ed.* **2004**, *43*, 1995–1998; *Angew. Chem.* **2004**, *116*, 2029–2032.
[3] F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, *Angew. Chem. Int. Ed.* **2000**, *39*, 2362–2364; *Angew. Chem.* **2000**, *112*, 2452–2454.
[4] a) T. Drews, W. Koch, K. Seppelt, *J. Am. Chem. Soc.* **1999**, *121*, 4379–4384; b) R. J. Gillespie, M. J. Morton, *Inorg. Chem.* **1970**, *9*, 811–814.
[5] K. O. Christe, R. Bau, D. Zhao, *Z. Anorg. Allg. Chem.* **1991**, *593*, 46–60.
[6] J. Passmore, G. Sutherland, P. S. White, *Inorg. Chem.* **1981**, *20*, 2169–2171.
[7] H. Hartl, J. Nowicki, R. Minkwitz, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 328–329; *Angew. Chem.* **1991**, *103*, 311–312.
[8] A. Apblett, F. Grein, J. P. Johnson, J. Passmore, P. S. White, *Inorg. Chem.* **1986**, *25*, 422–426.
[9] J. M. Michaud, M. C. L. Gerry, *J. Am. Chem. Soc.* **2006**, *128*, 7613–7621.
[10] E. P. L. Hunter, S. G. Lias, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.
[11] A. Y. Rogachev, R. Hoffmann, *J. Am. Chem. Soc.* **2013**, *135*, 3262–3275.
[12] N. G. Adams, D. Smith, M. Tichy, G. Javahery, N. D. Twiddy, E. E. Ferguson, *J. Chem. Phys.* **1989**, *91*, 4037.
[13] F. Cacace, G. de Petris, F. Pepi, M. Rosi, A. Sgamellotti, *J. Phys. Chem. A* **1998**, *102*, 10560–10567.
[14] T. A. Engesser, M. R. Lichtenthaler, M. Schleep, I. Krossing, *Chem. Soc. Rev.* **2016**, *45*, 789–899.
[15] a) I. Krossing in *Comp. Inorg. Chem. II*, Elsevier, **2013**; b) I. Krossing, I. Raabe, *Angew. Chem. Int. Ed.* **2004**, *43*, 2066–2090; *Angew. Chem.* **2004**, *116*, 2116–2142.
[16] I. Krossing, *J. Am. Chem. Soc.* **2001**, *123*, 4603–4604.
[17] A. Reisinger, N. Trapp, I. Krossing, S. Altmannshofer, V. Herz, M. Presnitz, W. Scherer, *Angew. Chem. Int. Ed.* **2007**, *46*, 8295–8298; *Angew. Chem.* **2007**, *119*, 8445–8449.
[18] P. J. Malinowski, I. Krossing, *Angew. Chem. Int. Ed.* **2014**, *53*, 13460–13462; *Angew. Chem.* **2014**, *126*, 13678–13680.
[19] A. J. Lehner, N. Trapp, H. Scherer, I. Krossing, *Dalton Trans.* **2011**, *40*, 1448–1452.
[20] T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing, *Angew. Chem. Int. Ed.* **2012**, *51*, 6529–6531; *Angew. Chem.* **2012**, *124*, 6635–6637.
[21] T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 8139–8143; *Angew. Chem.* **2010**, *122*, 8316–8320.
[22] I. Krossing, A. Reisinger, *Coord. Chem. Rev.* **2006**, *250*, 2721–2744.
[23] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490–502.
[24] A. Decken, C. Knapp, G. B. Nikiforov, J. Passmore, J. M. Rautiainen, X. Wang, X. Zeng, *Chem. Eur. J.* **2009**, *15*, 6504–6517.
[25] G. A. Olah, G. K. S. Prakash,, G. Rasul, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 6716–6720.
[26] L.-H. Chen, E. M. Nour, J. Laane, *J. Raman Spectrosc.* **1983**, *14*, 232–235.
[27] C. G. Davies, R. J. Gillespie, P. R. Ireland, J. M. Sowa, *Can. J. Chem.* **1974**, *52*, 2048–2052.
[28] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9–15.
[29] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735.
[30] C. Ehrhardt, R. Ahlrichs, *Theor. Chim. Acta* **1985**, *68*, 231–245.
[31] CCDC 1434970-1434973 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre..

Received: April 18, 2016
Revised: June 10, 2016