A “Silver” Bond?

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Experimental Detection and Properties of $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$ by Rotational Spectroscopy**

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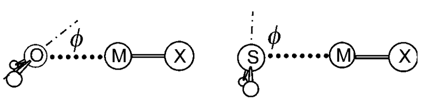
We report the first generation and characterization of two simple compounds formed by the interaction of either H_2O or H_2S with AgCl, namely $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$. They were observed in the gas phase by rotational spectroscopy. The AgCl is produced by laser ablation of metallic silver in the presence of CCl_4 and then picks up an H_2O or H_2S molecule.

AgCl is known, from interpretation of its Cl nuclear quadrupole coupling constant, to have a fractional ionic character of approximately 0.7, so that it has significant ion-pair character.[1] The interaction of AgCl with H_2O molecules, and in particular one H_2O molecule, is of fundamental chemical interest because the H_2O molecules have the opportunity to interact with an incipient Ag^+ ion. How does this interaction differ from those of H_2O with the less polar, covalent Lewis acids HCl and ClF (fractional ionic characters of 0.25 and 0.35)?

The hydrogen- and halogen-bonded complexes $H_2O\cdots H{-}Cl$ and $H_2O\cdots Cl{-}F$ have each been investigated in the gas phase by rotational spectroscopy as part of an extensive systematic program. $H_2O\cdots H{-}Cl$ and $H_2O\cdots Cl{-}F$ have equilibrium geometries of C_s symmetry,[2,3] with a pyramidal configuration at O when HCl or ClF forms either a hydrogen or halogen bond to that atom (see Figure 1). In each case, however, there is a low potential-energy barrier to the planar, C_{2v} geometry so that even in the zero-point state the molecule is inverting and is effectively planar. On the other hand, in the analogous pair of complexes $H_2S\cdots H{-}Cl$ and $H_2S\cdots Cl{-}F$ the potential energy barrier is high enough to ensure that each has a permanently pyramidal configuration at S,[4,5] with HCl or ClF forming a weak bond to S at approximately 90° to the H_2S subunit, as shown in Figure 1. These angular geometries, and those of many other hydrogen- and halogen-bonded complexes, can be rationalized by means of some simple empirical rules.[6,7] For both H_2O and H_2S acting as Lewis bases, the electrophilic ends $^{\delta+}H$ and $^{\delta+}Cl$ of the weakly polar molecules HCl and ClF, respectively, are assumed to seek the axis of a nonbonding electron pair carried by the base. A further question is: Are the angular geometries of the resulting molecules $H_2Y\cdots Ag{-}Cl$ isomorphic with those of $H_2Y\cdots H{-}Cl$ and $H_2Y\cdots Cl{-}F$ ($Y = O$ or S), indicating that the empirical rules are also obeyed when AgCl is the Lewis acid? All $B\cdots M{-}X$ ($B = CO$, $M = Cu$,[8] Ag,[9] Au[10]) have a linear arrangement similar to those in $OC\cdots H{-}Cl$[11] and $OC\cdots Cl{-}F$.[12] Thus, in all these systems, the Lewis acid attaches along the axis of the n-pair on C. A linear geometry was also found in $N_2\cdots Cu{-}F$.[13]



MX	ϕ[deg.]
HCl	36.3(3)
ClF	58.9(16)
AgCl	42(5)

MX	ϕ[deg.]
HCl	93.8(5)
ClF	95.8(5)
AgCl	78.7(8)

Figure 1. Angular geometries of several $H_2Y{-}M{-}X$ compounds; -•-• indicates the local C_2 axis of the H_2O or H_2S subunit.

Observed rotational transitions of both $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$ were characteristic of a nearly prolate asymmetric rotor of large *A* value having only *a*-type transitions, which exhibit Cl nuclear quadrupole hyperfine structure. For $H_2O\cdots Ag{-}Cl$, R-branch $K_{-1} = 1$ transitions of the type $(J+1)_{1,J+1}\leftarrow J_{1,J}$ and $(J+1)_{1,J}\leftarrow J_{1,J-1}$ were observed in addition to the $(J+1)_{0,J+1}\leftarrow J_{0,J}$ series and for a given *J* were more intense than those having $K_{-1} = 0$. This observation confirms that the molecule has a pair of equivalent H nuclei exchanged by a rotation C_2 about the *a* axis and therefore that the equilibrium geometry of $H_2O\cdots Ag{-}Cl$ is either C_{2V} planar at equilibrium or C_s pyramidal but with a potential-energy barrier to planarity low enough that the $v = 0$ and 1 states associated with the motion that inverts the configuration at the O atom are well separated. For $H_2S\cdots Ag{-}Cl$ only the $(J+1)_{0,J+1}\leftarrow J_{0,J}$ series could be detected despite a careful search, an observation consistent with a pyramidal configuration at the S atom and no inversion on the microwave timescale. The reason for the different behavior with respect to inversion is presumably that $H_2S\cdots Ag{-}Cl$ is more strongly bound than $H_2O\cdots Ag{-}Cl$ (see below) and that there is a much larger angle between the n-electron pairs on S than on O. The result is a higher and wider barrier to inversion in $H_2S\cdots Ag{-}Cl$.

The usual arguments show that for $H_2O\cdots Ag{-}Cl$ in the ground state the $K_{-1} = 1$ levels occur in combination with the three symmetric proton spin functions while the $K_{-1} = 0$ levels combine with the single antisymmetric function. Moreover, population transfer from $K_{-1} = 1$ levels into $K_{-1} = 0$ levels during the supersonic expansion is hindered by a collisional propensity rule[14] which forbids triplet state ($K_{-1} = 1$) to

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singlet state ($K_{-1}=0$) transitions. Hence, the lower J, $K_{-1}=1$ levels retain their significant population. The wave-number separation between the $K_{-1}=0$ and 1 levels of a given J is only a few cm^{-1}. Thus, given their 3:1 nuclear spin weight advantage, the $K_{-1}=1$ levels have a greater population, which is retained in the jet, and the $K_{-1}=1$ transitions are stronger. The statistical weight ratio changes to 1:2 for $D_2O\cdots Ag{-}Cl$, so that the $K_{-1}=0$ transitions should be the stronger, as was observed. If, on the other hand, the barrier to inversion at S in $H_2S\cdots Ag{-}Cl$ is sufficiently high, there is no inversion, and the $v=0$ and 1 levels become degenerate. Since no collisional propensity rule forbids transfer of population between the levels ($v=0$, $K_{-1}=1$) and ($v=1$, $K_{-1}=0$) or between ($v=1, K_{-1}=1$) and ($v=0, K_{-1}=0$), the population is drained from the $K_{-1}=1$ levels during the expansion.

Spectral analysis led to the rotational constants, centrifugal distortion constants, and Cl nuclear quadrupole coupling constants recorded in Table 1 for various isotopologues of $H_2O\cdots Ag{-}Cl$, and $H_2S\cdots Ag{-}Cl$. The quantities $B+C$, $B-C$, Δ_J, Δ_{JK}, χ_{aa} and $\chi_{bb}-\chi_{cc}$ were determinable for $H_2O\cdots Ag{-}Cl$, but for $H_2S\cdots Ag{-}Cl$ the absence of $K_{-1}=1$ transitions ensured that only $B+C$, Δ_J, and χ_{aa} were available. The fact that B and C differ by only approximately 8 MHz for the $H_2O\cdots Ag{-}Cl$ isotopologues is strong evidence for a linear arrangement of the atoms $O\cdots Ag{-}Cl$, with only the H atoms off this axis. Likewise, the value $\chi_{bb}-\chi_{cc}\approx 0$ is consistent with this conclusion, showing that the cylindrical symmetry of the electric field gradient at Cl is retained. Similar arguments cannot be used for $H_2S\cdots Ag{-}Cl$ because the required differences in the constants are unavailable. For both $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$, the small changes in rotational constants when ^{107}Ag is substituted by ^{109}Ag show that the silver atom lies close to the center of mass (the assignment of rotational constants to the ^{107}Ag and ^{109}Ag isotopologues was confirmed by using a sample of ^{107}Ag-enriched silver foil). Conversely, the large changes when H is substituted by D and ^{35}Cl by ^{37}Cl show that the H and Cl atoms must be at the extreme ends in both these molecules. Given these arguments and those based on nuclear spin statistical weights/rotational cooling, the geometries of the two molecules must be of the general type shown in Figure 1.

Quantitative geometries can be determined from the isotopic data presently available only by making some assumptions. The proximity of Ag to the center of mass means that this atom cannot be located with the available data for either molecule and thus that the distances $r(Y\cdots Ag)$ ($Y=O$ or S) and $r(Ag{-}Cl)$ are highly correlated. We therefore use the following approach. We assume that the r_0 geometries[15,16] of H_2O and H_2S are unchanged when $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$, respectively, are formed. The results given below are relatively insensitive to small changes in the H_2Y geometries. The distance $r(\text{Ag-Cl})=2.2548(6)$ Å for $OC\cdots Ag{-}Cl$ has been determined by Walker and Gerry[9] and is shortened by approximately 0.025 Å relative to free AgCl. The distance $r(Ag{-}Cl)$ in the $H_2Y\cdots Ag{-}Cl$ is unlikely to differ from this value by more than ± 0.02 Å because the interactions of H_2O and H_2S with AgCl are likely to be of strength similar to that involving CO in $OC\cdots Ag{-}Cl$. Accordingly, least-squares fits of the rotational constants for the various isotopologues shown in Table 1 (B and C for $Y=O$ and $B+C$ for $Y=S$) were carried out with $r(Ag{-}Cl)$ fixed at 2.2548 ± 0.02 Å using the program STRFIT[17] to give the distances $r(Y\cdots Ag)$ and the angles ϕ (as defined in Figure 1). The results for ϕ and $r(Y{-}Ag)$ were as follows: $Y=O$: 42(5)° and 2.229(35) Å; $Y=S$: 78.7(8)° and 2.399(21) Å.

The strength of the interaction between either H_2O or H_2S and AgCl can be gauged by the intermolecular stretching force constant k_σ, which can be determined from the centrifugal distortion constant Δ_J if it can be assumed that the intermolecular stretching mode is significantly lower in wavenumber than other stretching modes in the molecule. Using the appropriate expression from Millen,[18] the results are $k_\sigma=37$ and $63\,\mathrm{N\,m^{-1}}$ for $H_2{}^{16}O\cdots{}^{107}Ag{-}{}^{35}Cl$ and $H_2{}^{32}S\cdots{}^{107}Ag{-}{}^{35}Cl$, respectively. The values of this quantity for $H_2O\cdots H{-}Cl$ and $H_2O\cdots Cl{-}F$ are 12.5 and $14.2\,\mathrm{N\,m^{-1}}$ while for $H_2S\cdots H{-}Cl$ and $H_2S\cdots Cl{-}F$ they are 6.8 and $13.3\,\mathrm{N\,m^{-1}}$, respectively.[7] Thus, according to the k_σ criterion, $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$ are more strongly bound than their hydrogen and halogen-bonded analogues, but these results should be treated cautiously because the $Ag{-}Cl$ bonds are likely to have similar stretching force constants to the $O\cdots Ag$ or $S\cdots Ag$ bonds. Nevertheless, it is clear that the geometries of $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$ are isomorphic with those of their hydrogen- and halogen-bonded counterparts. Is there a silver bond analogous to the more familiar hydrogen and halogen bonds?

Table 1: Observed spectroscopic constants of isotopologues of $H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$.

Isotopologue	($B+C$) [MHz]	($B-C$) [MHz]	Δ_J [kHz]	Δ_{JK} [kHz]	χ_{aa}(Cl)[MHz]	($\chi_{bb}-\chi_{cc}$)(Cl) [MHz]
$H_2O\ {}^{107}Ag^{35}Cl$	3837.23586(46)	8.36795(27)	0.3834(89)	39.89(13)	−32.3193(53)	−0.498(28)
$H_2O\ {}^{109}Ag^{35}Cl$	3835.58844(94)	8.35932(56)	0.382(18)	40.01(27)	−32.319(11)	−0.516(56)
$H_2O\ {}^{107}Ag^{37}Cl$	3723.09204(52)	7.87817(32)	0.3644(94)	37.19(14)	−25.491(18)	−0.50(12)
$H_2O\ {}^{109}Ag^{37}Cl$	3721.19978(34)	7.86931(26)	0.3688(64)	37.18(10)	−25.496(15)	−0.372(68)
$D_2O\ {}^{107}Ag^{35}Cl$	3598.6457(11)	13.85268(68)	0.343(21)	68.00(33)	−32.325(37)	−0.58(26)
$D_2O\ {}^{109}Ag^{35}Cl$	3597.6055(16)	13.84320(92)	0.344(29)	68.21(45)	−32.341(52)	−0.63(37)
$H_2S\ {}^{107}Ag^{35}Cl$	2681.92031(13)	–	0.1730(13)	–	−29.4495(19)	–
$H_2S\ {}^{109}Ag^{35}Cl$	2681.92926(24)	–	0.1758(24)	–	−29.4445(35)	–
$H_2S\ {}^{107}Ag^{37}Cl$	2610.77674(36)	–	0.1574(31)	–	−23.271(49)	–
$H_2S\ {}^{109}Ag^{37}Cl$	2610.78552(32)	–	0.1705(28)	–	−23.178(44)	–
$D_2S\ {}^{107}Ag^{35}Cl$	2579.58496(24)	–	0.1643(21)	–	−29.454(33)	–
$D_2S\ {}^{109}Ag^{35}Cl$	2579.57188(32)	–	0.1633(27)	–	−29.476(45)	–

Experimental Section

$H_2O\cdots Ag{-}Cl$ and $H_2S\cdots Ag{-}Cl$ were produced in the Fabry-Perot cavity of a pulsed-jet, FT microwave spectrometer fitted with a laser-ablation source suited to the production of metal compounds, the details of which are given elsewhere.[19] A mixture composed of argon at a partial pressure of 6 bar, carbon tetrachloride at its room-temperature vapor pressure, and either water at its vapor pressure or hydrogen sulfide at a partial pressure of 0.2 bar was pulsed from a solenoid valve over the surface of a slowly rotating silver rod that was ablated by a suitably delayed approximately 20 mJ pulse of 532 nm radiation from a Nd:YAG laser. The ablated metal reacts with CCl_4 to produce AgCl, which subsequently picks up a molecule of H_2O or H_2S to form either $H_2O\cdots Ag{-}Cl$ or $H_2S\cdots Ag{-}Cl$, respectively. These molecules, entrained in argon, then expand into the Fabry-Perot cavity of the spectrometer where rotational transitions are observed and their frequencies measured, as described previously.[19]

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