A Five-Coordinate Compound with Inverted Ligand Field: An Unprecedented Geometry for Silver(III)

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Dedicated to Dr. F. Martínez-Buenaga on the occasion of his 75th birthday

Abstract: By using suitable synthetic procedures, we have first isolated the square-planar organosilver(III) compounds [PPh₄] [(CF₃)₂AgX₂] [X = Cl (1a), Br (2a)]. The geometry and stereochemistry of the chloro-derivative 1a have been unambiguously established by single-crystal X-ray diffraction (SC-XRD) methods. Following our calculations on the relative stability of the cis-trans-[CF₃AgX]⁻ couples (X = F, Cl, Br, I), the experimentally obtained compounds 1a and 2a appear to be kinetically favored stereoisomers. They display some unexpected coordination modes. In particular, this five-coordinate species also exhibits an inverted ligand field.

Oxidation state III is the highest currently available for silver. Nearly all Ag₃ compounds are diamagnetic and show square-planar (SP-4) geometry, as exemplified (Scheme 1) by the fluoro-complex [AgF₃]⁻ and by the homoleptic organometallic complexes [AgR₄]⁻ (R = CHF₂). These prototypical compounds are stabilized by small monodentate ligands with no steric constraints that might bias the preferred geometry. Different geometries are hardly ever found for this 4d⁻ ion, and the few departing cases are invariably based on the tetragonal symmetry (Scheme 1). In the square pyramidal (SP-5: τ < 0.1) structure of the neutral complex (CF₃)₂Ag(phen), the fairly long apical Ag···N separation (> 240 pm) induces little distortion in the nearly SP-4 basal plane; the observed overall arrangement might well be favored by the rigid bidentate phen ligand. In the chain-like structure of AgF₃, the loose axial Ag···F interactions (254.0(4) pm) established between adjacent chains result in an elongated octahedral geometry, which can also be described as square bipyramidal (SBPY-6).[10] Finally, a regular octahedral environment (OC-6) for Agiii is most certainly attained in the paramagnetic double perovskite Cs₂K[AgF₆], which is isomorphous with the Cs₂K[CaF₆] homologue.[12]

The structure of mononuclear AgF₃ (Scheme 2) both in inert matrixes (IR spectroscopy) and in the gas phase (calculated) is again a square with a vacant site (T shape, Cs₂). A symmetric trigonal arrangement (D₃h) is prevented by Jahn–Teller distortion.[16] The structures calculated for the heavier-halide AgX₃ homologues (X = Cl, Br, I) are better described as XAg₂X₄ adducts (Scheme 2) involving reduction to Ag¹⁺. This tendency to undergo reduction explains why the vast majority of Agiii compounds currently isolated are stabilized by hard ligands with first-row donor atoms (C, N, F) and why none of the heavier binary halides AgX₃ or related [AgX₄]⁺ complexes have been prepared to date.

In our effort to assay the stabilizing ability of the CF₃ ligand, we recently isolated the whole series of halide complexes [PPh₄][(CF₃)₂AgX] (X = F, Cl, Br, I). Now, we report on the remarkable tendency of the related [trans-}

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(CF$_3$)$_2$AgX$_2$\(^{+}\) anions to associate an additional X- ligand to afford [(CF$_3$)$_2$AgX$_3$]\(^{-}\) complexes, with the bromo-derivative [PPh$_4$][(CF$_3$)$_2$AgBr$_3$] showing unprecedented trigonal geometry. The analysis of its electronic structure reveals this novel compound as a singular five-coordinate species with inverted ligand field.

The slow addition of the homoleptic organosilver(i) compound [PPh$_4$][(CF$_3$)$_2$AgCF$_3$] (A)\[^{[5]}\] dissolved in CH$_2$Cl$_2$ to a solution of Cl$_2$ in CCl$_4$/CH$_2$Cl$_2$ at -78 °C affords the oxidized compound [PPh$_4$][(trans-(CF$_3$)$_2$AgCl)$_2$] (1a) in nearly quantitative spectroscopic yield [\(^{[19]}\) F NMR]. In this process (Scheme 3), the order of addition of the reagents is crucial to avoid ligand rearrangement, which takes readily place if the oxidant is added onto A.\[^{[21]}\] No such rearrangement processes were observed working with the homologous gold system.\[^{[14]}\] Upon chlorination under the indicated conditions, the \(^{[19]}\)F NMR signal of the starting product A (\(\delta_F = -25.6\) ppm)\[^{[19]}\] is downfield shifted to \(\delta_F = -24.54\) ppm (Figure S4). More importantly, the \(J^{(109)}\)Ag,\(^{[19]}\)F coupling constant undergoes a dramatic reduction from 100.7 Hz in A to 14.0 Hz in 1a.\[^{[19]}\] The very small value denotes both oxidation of the metal centre and a trans arrangement of the CF$_3$ groups. Our spectroscopic parameters are in agreement with those reported by Eujen, Hoge and Brauer, who first observed complex 1a in solution, formed upon reaction of [PPh$_4$][(trans-(CF$_3$)$_2$AgCN)$_2$] with AcCl.\[^{[20]}\] Unfortunately, this reaction was so slow that decomposition processes and competing side-reactions producing undesired by-products could not be avoided. In turn, our simple and efficient procedure has enabled us to isolate complex 1a as a thermally unstable orange solid. According to its colour, compound 1a in Me$_2$CO solution at -50 °C shows a characteristic absorption at \(\lambda = 405\) nm in the visible region of the optical spectrum (Figure S3). The composition of the anion is determined by the appropriate isotopic distribution of the nominal peak in MS and confirmed by high-resolution mass spectrometry (HRMS): 314.8339 Da.

The stereochemistry of 1a (Figure 1) was unambiguously established by single-crystal X-ray diffraction (SC-XRD).\[^{[21]}\] Since the Ag atom is located at an inversion center, the Cl-Ag-Cl and CF$_3$-Ag-CF$_3$ units are perfectly linear (imposed by symmetry). The Ag-C distance, 213.7(3) pm, is in the longest edge found in organosilver(III) compounds,\[^{[17]}\] being comparable to that found in the highly distorted porphyrinoid compound Ag[N(C)]$_2$: 212.6(2) pm.\[^{[22]}\] In line with this elongated Ag-C bond is the low value of \(J^{(109)}\)Ag,\(^{[19]}\)F observed in solution. In contrast, the Ag-Cl distance, 228.68(8) pm, is significantly shorter than in the only precedent described to date, namely [PPh$_4$][(CF$_3$)$_2$AgCl]: 232.03(4) pm.\[^{[21]}\] This difference evidences the marked trans influence of the CF$_3$ ligand\[^{[20]}\] operating in the latter compound. Accordingly, the \(\nu\)(Ag-Cl) band observed in the IR spectrum of 1a (B$_{1u}$: 386 cm$^{-1}$) appears at higher frequency than found for [PPh$_4$][(CF$_3$)$_2$AgCl] (A$_2$: 348 cm$^{-1}$).\[^{[17]}\]

The bromo-derivative [PPh$_4$][(trans-(CF$_3$)$_2$AgBr)$_2$] (2a) was obtained by reaction of A with Br$_2$ following a similar procedure as indicated above. It was isolated as a thermally unstable, dark orange solid characterized by an absorption at \(\lambda = 405\) nm in the visible region of the electronic absorption spectrum in Me$_2$CO solution at -50 °C (Figure S3). The substantial red-shift observed with respect to 1a suggests that these absorptions are ligand-to-metal charge-transfer (LMCT) bands associated with lone pairs (np) on the halide X ligands. The \(^{[19]}\)F NMR signal of 2a (\(\delta_F = -16.14\) ppm) appears significantly deshielded with respect to 1a. The similar coupling constant to the metal center, \(J^{(109)}\)Ag,\(^{[19]}\)F = 18.1 Hz, also points to a trans stereochemistry.\[^{[20]}\] As in the previous case, the composition of the anion 2a is determined by the appropriate isotopic distribution of the nominal peak in MS and confirmed by HRMS: 402.7322 Da.

No oxidation is observed by reaction of A with I$_2$, under similar conditions and all our attempts to obtain the fluoro-derivative [PPh$_4$][(trans-(CF$_3$)$_2$AgF)$_2$] failed: By treating 1a with AgF, massive reduction to silver metal occurred, whereas treatment of A with XeF$_2$ in the solid state invariably resulted in explosion even at low temperatures. Nevertheless, the whole series of stereoisomers [(trans-(CF$_3$)$_2$AgX)$_2$] (X = F, Cl, Br) were identified as local minima by DFT calculation (Figure S13). We also found that the isomeric species [cis-(CF$_3$)$_2$AgX]$_2$ were invariably more stable than their corresponding trans stereoisomers (Figure S14). The electronic structures of the [(trans-(CF$_3$)$_2$AgX)$_2$] stereoisomers reveal ligand-field inversion in all cases (Figure S15).\[^{[24, 25]}\] According to our calculations, our essays have led to the kinetically favored trans stereoisomers. Hence, we sought to promote isomerization to the thermodynamically favored cis stereoisomers. Owing to the low stability of compounds 1a and 2a, thermal activation was pointless. However, it was noticed that by redissolving freshly prepared solid samples of 2a in Me$_2$CO at -80 °C, a new signal appears in the \(^{[19]}\)F NMR spectra at \(\delta_F = -18.25\) ppm in minor ratio (1:20) with an associated \(J^{(109)}\)Ag,\(^{[19]}\)F = 52.96 Hz (Figure S5), which we tentatively assign to the stereoisomer [cis-(CF$_3$)$_2$AgBr$_2$] (2b). Both isomers decompose into BrCF$_3$ and [CF$_3$AgBr] (Figure S10). Compound 1a decomposed in a similar way.
Isomerization in $d^8$ square-planar $X_nML_2$ complexes is a thoroughly studied process.[24] In general, it occurs more readily with the heavier halides and is favored by the presence of Lewis bases.[26] However, the addition of $Br^-$ to solutions of $2a$ did not result in the desired isomerization. In turn, a significant broadening of the $^{19}F$ NMR signal suggested some kind of dynamic association (Figures S7 and S8). The association of an additional ligand had been suggested for some $Ag^+$ complexes in solution,[27] and the only two structural evidences contain the tetradentate ethylenedibiguane frame and are again based on a tetragonal symmetry.[28]

Aiming to find out the generality of the process, we have calculated the interaction of the whole series of $[trans-(CF_3)_2AgX_3]_2$ complexes ($X=F, Cl, Br, I$) with an additional $X^-$ ion by theoretical methods. Well-defined five-coordinate $[(CF_3)_2AgX_3]_2$ minima were located in all cases. The interaction is enthalpy-favored but is roughly balanced by the adverse entropic factor implied in every association process (Table 1). The optimized geometry for the fluoro-complex $[(CF_3)_2AgF_3]_2$ can be described as $SPY-5$ (Figure 2a), whereas the structures of the heavier homologues are all trigonal bipyramidal ($TPB r y-5$; Figures 2b and S16). In order to ascertain the reasons underlying this structural distribution are well below the HOMO and inverted in order with the ligands. The observed electronic structure is characterized by SC-XRD methods.[21] The Ag-C distances, 2.077(4) and 2.092(4) pm, are comparable to those observed in the homoleptic compound $[PPh_4][Ag(CF_3)_2]: 209.8(2)$ pm.[26] The $Ag-C$ bonds in $3$ are actually shorter than in the square-planar complex $1a$. The $Ag-Br$ distances (255.86(4), 256.69(5) and 265.16(4) pm) are all longer than that found in the square-planar complex $[PPh_4][(CF_3)_2AgBr]: 246.25(2)$ pm.[27] We would like to stress that five-coordination in $3$ is not sterically forced, since every ligand around the metal is monodentate. The overall geometry is surprisingly similar to that reported for the neutral gold(III) compound ($Me_2PClAuCl$), which exhibits a nearly regular $TPB r y-5$ geometry ($\tau=0.94$).[30] To the best of our knowledge compound $3$ is the first $Ag^+$ derivative with trigonal symmetry described to date.

A detailed analysis of the electronic structure of the $[(CF_3)_2AgBr]_2$- anion under imposed $D_{3d}$ symmetry (Figure 4)[31] reveals that the MOs with major metal contribution are well below the HOMO and inverted in order with respect to the standard arrangement derived from $D_{3d}$ ligand-field splitting.[32] Thus, the $a_1^+$ MO with mainly $d_z^2$ character, which is usually the highest lying orbital of the $d$ set, is here greatly stabilized. The significant contribution from the $F_3$ groups (34%) indicates an important degree of covalency in the $Ag-CF_3$ bond. Slightly above lie the degenerate $e'$ ($d_{x^2-y^2}$) and $e''$ ($d_{xy}$) pairs with roughly 10% contribution from the ligands. The HOMO is, in turn, mainly contributed by the ligands. The observed electronic structure is character-

\[
[(CF_3)_2AgBr_3]^- \rightarrow CF_3 + [(CF_3)Ag^+X^{-}]
\]

Table 1: $Energy$ involved in the interaction of $[trans-(CF_3)_2AgX_3]_2$ with an additional $X^-$ ligand in the indicated solvent.$[^{a}]$

| solvent  | $\Delta G$ | $\Delta H$ | $\Delta G$ | $\Delta H$ | $\Delta G$ | $\Delta H$ |
|----------|------------|------------|------------|------------|------------|------------|
| $Me_2CO$ | 4.4        | 3.2        | 1.6        | 7.5        | 1.2        | 9.5        |
| $MeCN$   | 4.1        | 4.8        | 0.3        | 8.7        | 2.4        | 10.7       |

$[^{a}]$ Values [kcal mol$^{-1}$] calculated at the DFT/M06/Def2-TZVPD level of theory.

Figure 2. Geometry of the anions $[(CF_3)_2AgF_3]^- (a) and [(CF_3)_2AgBr_3]^- (b)$ calculated in MeCN solution at the DFT/M06/Def2-TZVPD level. The whole set of $[(CF_3)_2AgX_3]_2$ anions is shown in Figure S16.

Figure 3. Displacement-ellipsoid diagram (50% probability) of the $[(CF_3)_2AgBr_3]^-$ anion as found in crystals of $3$ (a) and its projection along the C-Ag-C axis (b).
interaction. The trigonal structure of the \((\text{CF}_3)_2\text{AgBr}_3\)_2 anion in the gas phase with indication of each moiety contribution (%) to the most relevant valence MOs. Depicted are only the frontier orbitals and those with a significant metal contribution. A full version is shown in Figure S19.

Figure 4. Energy levels calculated for the symmetrised \(D_{2h}\) \((\text{CF}_3)_2\text{AgBr}_3\)_2 anion in the gas phase with indication of each moiety contribution (%) to the most relevant valence MOs. Depicted are only the frontier orbitals and those with a significant metal contribution. A full version is shown in Figure S19.

istic of an inverted ligand field, which is extremely rare in five-coordinate compounds\([24, 33]\).

In summary, the thermally unstable organosilver(III) dihalide complexes \([\text{PPPh}_4]_2\text{trans-} (\text{CF}_3)_2\text{AgX}_2\) \((X = \text{Cl (1a)}, \text{Br (2a)})\) exhibit substantial acidic (electrophilic) behavior, as they interact with additional \(X^-\) ligands. The interaction is dynamic in solution \((^{19}\text{F NMR})\). The structural characterization of \([\text{PPPh}_4]_2(\text{CF}_3)_2\text{AgBr}_3\) \((3)\) in the solid state (SCXRD) gives unambiguous experimental proof of direct Ag-Br interaction. The trigonal structure of the \((\text{CF}_3)_2\text{AgBr}_3\)_2 anion in compound 3 illustrates an anticipated plasticity of the Ag(III) coordination environment, which was hitherto entirely based on the tetragonal symmetry. This five-coordinate compound also exhibits inverted ligand field. The unusual electronic structure associated with an unprecedented structural change will certainly have important implications in the reactivity of silver(III), which is still underdeveloped.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: axial acidity · five-coordination · highest oxidation states · inverted ligand field · silver(III)

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