Electrospray ionization mass spectra of the reactions of NaAuBr₄ and related aurates with nucleophiles

Dear Sir,

Electrospray ionization mass spectra in the negative ion mode, ESI(−)/MS, of aqueous solutions of AuBr₄ at different pH values have been reported by us[1] confirming the rapid equilibria (speciation) that were observed by spectrophotometry[2−4] AuBr₄ and [AuBr₃(OH)]⁻ predominate at pH 4 and [AuBr₂(OH)₂]⁻ in neutral solutions. Independently, other authors have reported similar ESI mass spectra of [AuCl₃(OH)]₄⁻.[5] Thus, gold seems to be unique among all the elements of the periodic table, not only because of the properties of the metal, known from the beginning of mankind, and of the gold nanoparticles,[6,7] but also because gold(III) salts do not precipitate easily Au(OH)₃ under neutralization, particularly in the presence of anions such as bromide or cyanide.[8,9] With the aim of uncovering further features of aurate(III) ions, we carried out a series of MS experiments that are reported for the first time: (1) the characterization of commercially available samples of NaAuBr₄ and NaAuCl₄ at different pH values, (2) the detection by ESI(−)/MS of the exchanges of ligands (Cl/Br/CN) in aurates and (c) a study of the reactivity (or lack of reactivity) of NaAuBr₄ with alcohols, phenols, carbonyl compounds, 1,3-dicarbonyl or 1,3-dicarboxyl compounds, and oximes, also followed by ESI(−)/MS.

We first analyzed by ESI(−)/MS aqueous solutions of NaAuBr₄·H₂O and NaAuCl₄·2H₂O at different pH values. The spectra were recorded with an Agilent LC/MSD TOF instrument set under the following conditions: 20-V fragmentation voltage, 3500-V capillary voltage, 3 ml/min flow and capillary temperature of 350°C, with N₂ as the nebulization gas at 20 psi. Several spectra were also registered at lower temperatures (150°C) with the same results (although the sensitivity decreased). The solutions were prepared in milli-Q water, at 0.10 M concentrations, and were allowed to equilibrate until the pH value (Crison pH-meter) was stable. They were then diluted (1:100) with ultrapure water and injected immediately. At the beginning of this work, we examined the effect of this dilution (0.001 M); in spite of the expected fact that the pH values were closer to 7, the spectra were identical to those at 0.10 M. The halido-hydroxido exchanges must be slowed down by dilution (with initial reaction rates 10⁻⁴ times lower), which explains the relative intensities of the peaks were practically the same as those in the equilibria at 0.10 M.

In ultrapure water, the commercially available samples of NaAuBr₄·H₂O (from Alfa Aesar and from Strem) and NaAuCl₄·2H₂O (from Aldrich) have pH values below 3 (1.81, 1.70 and 2.49, respectively, at 0.1 M), and around one equiv of NaOH had to be added to neutralize the solutions to pH 7. By ESI(−), both samples of ‘NaAuBr₄ hydrate’ in pure water showed only an intense AuBr₄⁻ peak (see Fig. 1a), with insignificant amounts of Br⁻ (or aggregates containing this anion). Thus, samples sold as sodium tetrabromoaurate–hydrate may contain high percentages of H₂AuBr₄; this deserves a warning because some reactions assumed to be catalyzed by these gold(III) species could be actually promoted by the protons of H₂AuBr₄ that contaminated NaAuBr₄·H₂O. On the other hand, the solutions of NaAuCl₄·2H₂O in pure water showed some hydrolysis to H[AuCl₃(OH)] (Fig. 1c), and NaCl (signals of [NaCl2]⁻ were detected), which partially explains their acidic pH; again, it is worth noting that some reactions reported to be catalyzed by AuCl₄⁻ species could have been promoted by H[AuCl₃(OH)] present in samples of NaAuCl₄·2H₂O. The addition of NaOH to these AuX₄ samples, up to pH 8.5, caused the replacement of some halide ligands, but AuBr₄⁻ still remained (Fig. 1b), whereas AuCl₄⁻ disappeared almost completely (Fig. 1d; isotopic distributions are in agreement with the ³⁵Cl/³⁷Cl ratio). Apparently, chloro/chorido ligands were replaced easily by the hydroxo/hydroxido ligands. In spite of that, species [AuCl₃(OH)]₄⁻ were clearly observed. In sharp contrast, when we neutralized analogous aqueous solutions of trivalent cations other than AuIII, such as FeBr₄⁻ or FeBr₇⁻, InBr₄⁻ or InBr₅⁻ and LaBr₄⁻, the ESI(−) signals were lost, due to the immediate formation of insoluble hydroxides or hydrated oxides.

The addition of NaBr to a neutral aqueous solution of NaAuCl₄ (yellow) gave rise to the appearance of AuBr₄⁻ and/or tribromoaurate-containing species (characteristic wine-red color and typical ESI spectra). It was not necessary to add a large excess of bromide ions to shift the equilibrium to the right: with only 200 mol % of NaBr, albeit all species [AuBr₃Cl₄⁻] were detected, AuBr₄⁻ was already relatively abundant (see Fig. 2a); with 400 mol % of NaBr, most the chloride ions had been replaced by bromide ions (AuBr₃Cl₂⁻ not observed). More outstanding was the change observed by addition of NaCN to the wine-red solutions of AuBr₄⁻, since the color faded immediately with only 200 mol % of cyanide ions (Fig. 2b); with ≥300 mol %, Au(CN)₄⁻ was the exclusive species detected. Thus, aurates with mixed ligands (depicted within brackets in Scheme 1) are not particularly favored. Moreover, aurates with several bromo/bromido ligands are more stable than their analogous CI complexes, and cyano/cyanido–aurates even more (in fact, we could not replace cyano ligands by hydroxide ions, or any other ligands). Some of these reactions were studied…

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spectrophotometrically years ago, with results that ESI(−)/C0MS has now confirmed. We also show that ESI(−)/C0MS is a quick technique to gain further insight into these exchanges. Even though the study of the rates and/or equilibrium constants of formation of these anionic complexes is outside our interests, ESI(−)/C0MS not only allows for the reliable characterization of the species involved (speciation) but also might provide kinetic information and their relative stability order.

Once the main aurate species in solution were established, we examined their possible reactions with alcohols, phenols, aldehydes, ketones and 1,3-dicarbonyls (activated methylene compounds). Most experiments were carried out with bromoaurates instead of with chloroaurates or cyanoaurates. We chose bromoaurates because their neutral and basic solutions can be stored for a long time while chlorohydroxoaurates decompose (with formation of AuI and/or Au precipitates), because cyanoaurates are so stable that they do not react with nucleophiles and because bromoaurates have been hardly investigated. In aqueous CH3CN or in aqueous THF, at room temperature (RT), we observed that simple alcohols, aldehydes and ketones did not react with AuBr4− or with [AuBrn(OH)4−]. This was surprising at first sight, as primary and secondary alcohols are oxidized to aldehydes and ketones, respectively, by [AuCl3(OH)]− and AuCl4− in acetate-buffered aqueous media[10]; the explanation lies again in the greater kinetic and thermodynamic stability, in aqueous solutions, of [AuBrn(OH)4−]− with regard to [AuCln(OH)4−]. However, on heating in non-aqueous media, bromoaurates enter more easily in redox processes; in fact, heating of [Et4N][AuBr4] with acetone was used to prepare [Et4N][AuBr2] (with formation of bromoacetone).[11]

Phenol reacted with NaAuBr4 (at pH ≤ 7.0, where AuBr4− predominates), with disappearance of the wine-red color and bromination at the para position of the hydroxy group. When more NaAuBr4 was added, up to an equimolar ratio, AuBr4− solutions were previously set to pH 9.5 (that is, when [AuBr2(OH)3]− and [AuBr3(OH)]− were the major species in the medium, with a small percentage of AuBr4− remaining) and phenol was then added in CH3CN/H2O (as phenolate ion, to maintain pH 9), mainly [AuBr(OH)2(OPh)]− was detected by ESI(−)/MS (Fig 3a), with disappearance of [AuBrn(OH)4−]− (n = 2 and 3). Also, 4-methylphenol (p-cresol), when treated with [AuBrn(OH)4−]− (n = 2–4), maintaining pH 9, chiefly gave [AuBr(OH)2(OPh4Me)]−.

Figure 1. ESI(−) mass spectra of NaAuBr4: (a) without neutralization and (b) after neutralization with NaOH till pH 8.46. ESI(−)/MS of NaAuCl4 (c and d).

Figure 2. ESI(−) spectra of aqueous solutions from: (a) AuCl4− + 2 Br−; (b) AuBr4− + 2 − CN.

![Equilibria diagram](image)

Figure 3. ESI(−) mass spectra of: (a) phenol and [AuBr₃(OH)₄₋₉]⁻ (n = 2–4) at pH 9; (b) acetylacetone and AuBr₄⁺ (pH 7); the ‘quartet’ at m/z 310–316 is a fragmented species (tribromoacetone−hydrate derivative, see SI); (c) acetylacetone and [AuBr₃(OH)₄₋₉]⁻ (n = 2–4) at pH 9.

2,4-Pentanedione (acetylacetone, acacH) also reacted with AuBr₄⁺ (pH 7). To the best of our knowledge, there is only one related case reported, namely, the reduction of Bu₄N[AuCl₄] to Bu₄N[AuCl₃] by acetylacetate. ESI(−)MS indicated that AuBr₄⁻ and acacH gave [AuBr₃(acac)]⁻ (Fig. 3b). Thus, unlike the case of phenol, the expected complex could be observed at neutral pH values, but 30 min later AuBr₄⁺ had disappeared while fragmentation product(s) became predominant ([C₃H₆BrO₂H]⁻), tribromoacetone derivative(s) arising from Br transfer and deacetylation, see Supporting Information, SI). Bromination of the active methylene group was confirmed by NMR spectroscopy, while a gold mirror was formed in the vial. When the reaction was re-examined at pH 9 (that is, with [AuBr₃(OH)₄₋₉]⁻, n = 2–4, plus acac⁻), in CH₂CN/H₂O, the main anionic species were [AuBr₃(acac)]⁻ and [AuBr(acac)(OH)₂]⁻ (Fig. 3c).

In other words, acac-containing complexes with three and one bromo ligands were relatively more stable. Ionic complex [AuBr₃(acac)]⁻ can only come from AuBr₄⁺ + acac⁻, while [AuBr(OH)₂(acac)]⁻ must come from [AuBr₂(OH)₂]⁻ + acac⁻ and from [AuBr₂(OH)(acac)]⁻ + OH⁻. Diethyl malonate behaved similarly to acacH.

We also examined the reaction of NaAuBr₄ with ketoxime PhCH₂CH₂C(=NOH)CH₃ (3-phenyl-2-butanone oxime) by ESIMS. We had investigated reactions of oximes with AuX₃ but not with NaAuBr₄, which we report here for the first time. At acidic pH (NaAuBr₄ + HAuBr₄), there was no replacement of ligands, as well as no redox processes (unlike the previous cases of phenols and active methylene compounds, which may be explained by the greater tendency of phenol and acacH to undergo C-bromination). At pH 6.3 (NaAuBr₄), pH 8.5 (equilibrium mixture shown in Fig. 1b) and pH 9.5 (where, as already indicated, [AuBr₂(OH)₄]⁻ and [AuBr₃(OH)]⁻ were the major species), the substitution of one oximato for one bromo ligand was observed. All these aurate species did react, although AuBr₄⁺ did it more slowly. As in the cases of phenols and acetylacetone, only one ligand was incorporated, even with a large excess of oxime at basic pH.

Apparently, in aqueous media (aqueous CH₃CN or THF), only organic compounds with pKₐ values below 12–13, such as phenols, active methylene compounds and oximes, are capable to replace one and only one bromo ligand of these AuIII complexes at RT, but their behavior pattern is different. To summarize: (1) phenols are brominated with AuBr₄⁺, while phenolates and active methylene compounds, which may be explained by the greater tendency of phenol and acacH to undergo C-bromination. At pH 6.3 (NaAuBr₄), pH 8.5 (equilibrium mixture shown in Fig. 1b) and pH 9.5 (where, as already indicated, [AuBr₂(OH)₄]⁻ and [AuBr₃(OH)]⁻ were the major species), the substitution of one oximato for one bromo ligand was observed. All these aurate species did react, although AuBr₄⁺ did it more slowly. As in the cases of phenols and acetylacetone, only one ligand was incorporated, even with a large excess of oxime at basic pH.

In conclusion, we have elucidated by ESI(−)MS, for the first time, the nature and approximate ratios of aurates [Au₃X₄₋₉]⁻ that are quickly generated when NaAuX₄ is mixed with ions Y⁻ (where X and Y are Cl, Br, CN and/or OH ligands). The solubility...
and stability at different pH values of bromohydroxoaurates are exceptional. Also for the first time, reactions of NaAuBr₄ with several types of organic compounds, including phenols, active methylene compounds and oximes have been followed by ESI(-)MS. Species AuBr₄⁻, [AuBr₃(OH)]⁻ and [AuBr₂(OH)₂]⁻ do not react similarly with these nucleophiles. Unlike the [AuBr₄⁻]⁻ ionic complexes, species such as [AuBr₂(OR)₂]⁻ and [AuBr(OR)₃]⁻ (with two or three alkoxido, phenolato, acetylacetonato or oximato ligands) have not been detected.

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Yours,

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References


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