Highlighting metallic behaviors of astatine in solution with O, S and N model ligands

F. BASSAL[1], M. SEYDOU[2], J. CHAMPION[3], A. SABATIE-GOGOVA[4], J.-Y. LE QUESTEL[1], G. MONTAVON[2], N. GALLAND[1]

[1] *Laboratoire CEISAM, UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France*
[2] *Laboratoire ITODYS, UMR 7086, Université Denis Diderot (Paris VII), Bâtiment LAVOISIER, 15 rue Jean Antoine de Baïf, 75205 PARIS CEDEX 13, France*
[3] *Laboratoire SUBATECH, UMR CNRS 6457, Ecole des Mines de Nantes, 4 rue A. Kastler, BP 20722, 44307 Nantes Cedex 3, France*
[4] *Cyclotron ARRONAX, 1, rue Aronnax, 44817 Saint-Herblain Cedex*
fadel.bassal@univ-nantes.fr

Astatine (At, Z=85: $[Xe]4f^{14}5d^{10}6s^{2}6p^{5}$) is the last known halogen in the periodic table. One of its longest-lived isotopes, ^{211}At, is of considerable interest as a potential radiotherapeutic agent for alpha-therapy[1], due to the energy and nature of the emitted particles. Since there is no stable isotope of astatine, many of the basic chemical studies with this chemical element have unfortunately been set aside[2]. Although located below iodine, the chemical similarities of At with the halogen group are not always obvious. Indeed, it is clear that the development of targeted radiotherapy agents based on At needs to gain a better understanding of its basic chemistry in aqueous solution. Recent studies showed that astatine presents a metal-like behavior when existing under the oxidation states +I and +III as At^{+} and AtO^{+} species[3]. However, at the present time, the number of studies dealing with the complexation properties of the cationic forms of astatine remains limited[4], owing to its low availability.

This work, based on an approach combining theoretical and experimental studies[5], aims at studying the complexation of the AtO^{+} cationic form with different heteroatomic (N, S, O) model ligands. As astatine is a heavy element, the quantum calculations used a two-component relativistic approach (SO-DFT) to reproduce the influence of spin-orbit coupling on At properties. Solvent effects are simulated through an implicit solvation model (UAHF) completed with specific parameters for At cavities. The computed equilibrium constants have been confronted with the experimental ones. The comparison reveals an outstanding coherence between both sets of values. This allowed us identifying the nature of the AtO^{+} binding with heteroatomic ligands, which could not be obtained experimentally from spectroscopic tools. A large variety of interactions have been evidenced together with a specific reactivity against carbon atoms in case of aromatic ligands. Finally, the key role of the solvent on the elemental chemistry of astatine has been highlighted.

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