

Letter to the Editor

## Comments on the Electronic Spectrum of Univalent Bismuth in Aqueous Solution

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In a recent article in this journal<sup>1</sup> we presented spectroscopic data on the Bi–BiCl<sub>3</sub>–HCl–H<sub>2</sub>O system which we, in the light of previous work on the similar molten salt system Bi–BiCl<sub>3</sub>, interpreted as being strongly indicative of the formation of univalent bismuth species stable in aqueous solution. It has subsequently come to our knowledge<sup>2</sup> that this article contains an error regarding the ground-state electron configuration of the univalent bismuth ion, Bi<sup>+</sup>. According to the theoretical investigation by Davis *et al.*,<sup>3</sup> which was cited by us, the ground state of Bi<sup>+</sup> is <sup>3</sup>P<sub>0</sub> in the whole range of ligand field strengths examined, not <sup>3</sup>P<sub>1</sub> or <sup>3</sup>P<sub>2</sub> as was erroneously stated in our article. The error stems from a misreading of a figure in the article by Davis *et al.* and it unfortunately managed to propagate through the entire preparation of our manuscript. The erroneously assumed ground state has some consequences for the interpretation of our data. First, the high-spin/low-spin duality of Bi<sup>+</sup>, which was proposed by us to account for the very different spectral characteristics of Bi<sup>+</sup> in various media, cannot be substantiated directly experimentally by magnetic methods, since the <sup>3</sup>P<sub>0</sub> level most probably is ESR-silent and diamagnetic [the compound (Bi<sup>+</sup>)(Bi<sub>9</sub><sup>5+</sup>)(HfCl<sub>6</sub><sup>2-</sup>)<sub>3</sub> has indeed been found to be diamagnetic].<sup>4</sup> Second, the identification of the two observed UV/vis bands with the two Bi<sup>+</sup> transitions <sup>3</sup>P<sub>1</sub> ← <sup>3</sup>P<sub>0</sub> and <sup>3</sup>P<sub>2</sub> ← <sup>3</sup>P<sub>0</sub> in a *very weak* and/or highly symmetrical ligand field must be addressed. In the gas-phase spectrum of Bi<sup>+</sup> these two absorptions are reported at 750 and 587 nm, respectively.<sup>5</sup> The two possible triplet–singlet transitions <sup>1</sup>D ← <sup>3</sup>P<sub>0</sub> and <sup>1</sup>S ← <sup>3</sup>P<sub>0</sub> are found in the UV region at 294 and 226 nm. The positions of the gas-phase triplet–triplet absorptions should be compared with those at 535 and 510 nm (at room temperature) reported by us. Therefore, the assumption of a Bi<sup>+</sup> ion in

a weak and/or highly symmetrical ligand field accounts for the number of absorption bands observed by us and very roughly also for the positions. However, the agreement between the aqueous and the gas-phase data is not good enough to be conclusive. Although no *direct* experimental evidence for high-spin/low-spin duality can be presented, there is thus still a reason to ponder on the possibility of a low-spin state of Bi<sup>+</sup>. A low-spin state of Bi<sup>+</sup> would require a singlet term to drop below the triplet states in energy. The separation of 30 000 cm<sup>-1</sup> between the <sup>1</sup>D<sub>2</sub> and <sup>3</sup>P<sub>0</sub> levels in the gas phase renders such a situation unlikely in the system discussed here, since the Bi<sup>+</sup> ion is probably *weakly* coordinated to chlorobismuthate(III) ions.

In addition to the extreme low- and high-ligand field cases of p–p transitions in Bi<sup>+</sup> discussed above, there is a third possible explanation for the observed UV/vis spectrum that has to be considered, namely that the bismuth species present is of the form [Bi<sup>+</sup> · nBi<sup>3+</sup>], n > 0. As pointed out by Corbett *et al.*,<sup>6</sup> the thermodynamic measurements which have been used to determine the species equilibria in Bi–BiCl<sub>3</sub> systems (results used by us to infer the existence of Bi<sup>+</sup>), cannot be used to determine the number n. For hypothetical species with n > 2 the resulting charge seems unrealistically high. However, the case n = 1 (i.e. Bi<sub>2</sub><sup>4+</sup>) would *a priori* be a reasonable candidate. We have therefore performed a theoretical study of this species in order to obtain information regarding its stability. The calculations were performed using the GAUSSIAN92 program package<sup>7</sup> employing the basis set by Stevens *et al.*<sup>8</sup> augmented with d-polarization functions (exp: 0.170). The basis set uses average relativistic core potentials, but spin–orbit coupling is not explicitly taken into account. This basis set has previously been shown to give consistent data in agreement with experiment for Bi<sub>5</sub><sup>3+</sup> and isoelectronic clusters.<sup>9</sup> The calculations unambiguously infer that Bi<sub>2</sub><sup>4+</sup> is unstable with

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respect to the dissociation into  $2 \text{Bi}^{2+}$  in the absence of stabilizing ligands. This result, in turn, strongly suggests that the number  $n$  in  $[\text{Bi}^+ \cdot n\text{Bi}^{3+}]$  is indeed equal to zero.

In summary, the UV/vis spectrum obtained from  $\text{BiCl}_3\text{-HCl(aq)}$  solutions reduced with bismuth metal is most readily attributed to the  $\text{Bi}^+$  ion subject either to a very strong ligand field of low symmetry (which in the extreme case could lead to a low-spin state) or, more likely, to a weak and/or highly symmetric field.

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