Univalent Bismuth. A Subvalent Main-Group Metal Ion Stable in Aqueous Solution

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Reduction of a saturated aqueous solution of bismuth(III) chloride in concentrated hydrochloric acid by bismuth metal at room temperature produces a scarlet solution with a single absorption band at 516 nm. The intensity of this absorption is found to decrease with increasing temperature. Comparison with visible spectroscopical data from earlier investigations strongly indicates that the reduced bismuth species formed is the univalent bismuth ion, Bi^+. No ESR signal is observable from the reduced solutions. This leads us to suggest the possibility of a ligand-field induced high-spin/low-spin duality of the s^2p^2 ion Bi^+, since previous spectroscopic work suggests a paramagnetic ground state of this ion in some molten-salt solvents. Raman spectra are inconclusive as to the nature of the subvalent bismuth species, but suggest that Bi^+ is coordinated by tetrachlorobismuthate(III) ions in aqueous solution.

Solubility studies give a Bi^+ concentration of 6.4 mM in a saturated solution, yielding a molar extinction coefficient of $1.3 \cdot 10^2$ M^{-1} cm^{-1} for this species.

In a paper published in 1908,[1] Denham presented evidence that bismuth metal is soluble in solutions of bismuth(III) chloride in aqueous hydrochloric acid. The author suggested (rather tentatively) that the subvalent species formed upon the dissolution is bivalent bismuth, Bi(II). Since this early report, no work seems to have been done on the subvalent chemistry of bismuth in aqueous solution, except for a few Russian articles dealing with the γ-induced radiolytical disproportionation of bismuth(III), in which Bi(II) and Bi(IV) are claimed to be the extremely unstable and short-lived reaction products.[2,3] Furthermore, the present authors know of no reports, since the days of Denham, on subvalent main-group metal ions (apart from Hg_2^{2+}) thermodynamically stable in aqueous solution.

This major hiatus in the exploration of bismuth chemistry is strange considering the enormous interest once stirred by the solutions of bismuth metal in liquid bismuth trihalides;[4,5] solutions in which bismuth is known to exist in oxidation states lower than three and from which the cluster cation Bi_9^{5+} may be isolated in the form of the compound $Bi_{24}Cl_{28} = (Bi_9^{5+})_2(BiCl_5^{2-})_4(Bi_2Cl_8^{2-})$.[6] Likewise, other Lewis-acidic molten salt systems have been shown to be suitable media for the synthesis of subvalent bismuth ions, the ones so far characterized being Bi^+, Bi_5^{3+} and Bi_8^{2+}.[7-10]

In this work, we report the reinvestigation of Denham's solution studies of bismuth metal in concentrated aqueous bismuth(III) chloride–hydrochloric acid solutions.

Experimental

Chemicals. Commercial $BiCl_3$ (Aldrich, $>98\%$) was sublimed twice under vacuum prior to use. Bismuth metal (Aldrich, 99.999%) and concentrated hydrochloric acid (Riedel-deHaen, p. A. grade) were used as received.

Analysis of $BiCl_3$–HCl stock solutions. The density of the saturated solution of $BiCl_3$ in concentrated hydrochloric acid was measured pycnometrically. The concentrations of chloride and bismuth were determined gravimetrically by precipitation of AgCl (from weighed samples of solution diluted with 1:1 HNO_3) and BiOCl (by dilution of weighed amounts of solution by a large excess of water), respectively.

Determination of the solubility of Bi in $BiCl_3$–HCl(aq). A carefully weighed amount of Bi was added to a known amount of $BiCl_3$–HCl solution in a vacuum-filtration apparatus, which was then evacuated. During the evacuation the apparatus was cooled to $-196\,°C$ in order to prevent loss of HCl and H_2O. The suspension was then stirred for a week, during which time the colour of the solution gradually changed from light green to bright scarlet.

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After this equilibration, the solution was filtered through the sintered glass disc of the apparatus under vacuum. After careful, repeated washings of the apparatus with concentrated HCl, followed by drying at 130°C, the apparatus was again weighed and the amount of dissolved Bi determined.

Raman spectroscopy. Raman spectra were recorded on a Bruker IFS-66/FRA-106 FT Raman spectrometer with a Ge-diode detector and a low-power Nd:YAG laser (wavelength 1064 nm) providing the exciting radiation. The resolution of the spectra was 4 cm^{-1}. The samples consisted of filtered solutions prepared as described above and transferred to the sample cells in a glove box under nitrogen. The cells were then sealed.

UV–VIS spectroscopy. Spectra were recorded on a Guided Wave 260 fiber optics spectrometer specially modified for work at high temperatures and pressures with samples contained in 5 mm circular cells. The optical path length of the NMR tubes used as sample cells in this work has previously been calibrated against standard UV–VIS cells and found to be 0.43 ± 0.01 mm. The samples were prepared as described above, transferred to the sample cells in the glove box and equilibrated for approximately 30 min at the appropriate temperature before the spectrum was recorded.

ESR spectroscopy. ESR spectra were recorded at room temperature on a Bruker ER-200D SRC instrument. Sample preparations were performed as described above.

Results and discussion

Solubility measurements. The density of the saturated $BiCl_3$–HCl(aq) stock solution was determined to be 2.74 g cm^{-3} and the concentration of Bi^{3+} and Cl^- to be 6.9 and 26.1 M, respectively. It is interesting to note that the stoichiometry of the saturated solution closely corresponds to a hydrated melt of formal composition $HBiCl_4 \cdot 3H_2O$. The dissolution of bismuth metal in this solution rapidly produces a bright scarlet colour, although the solubility is low at room temperature. The formal molar fraction of Bi with respect to $BiCl_3$ [i.e. $X_{Bi} = n_{Bi}/(n_{Bi} + n_{BiCl_3})$] in a saturated solution was found to be 9.2×10^{-4}. Although low, the metal solubility is greater than or comparable with the solubility of metal in the molten $M–MCl_n$ (M = Tl, Sn, Pb and Sb) systems.[11,12] When the saturated stock solution is diluted with hydrochloric acid the solubility of bismuth metal is rapidly reduced, as apparent from the disappearance of the characteristic scarlet colour.

ESR spectroscopy. The only signal observed was a very weak and broad feature at 3390 G (9.52 GHz spectrometer frequency). This feature was observed both in the stock solution and in the reduced solution, and is there-

fore assigned to traces of a paramagnetic impurity in the bismuth trichloride used, presumably a volatile transition metal halide such as $FeCl_3$. The absence of an ESR signal due to subvalent bismuth species effectively rules out the possibility that the reduced species formed is Bi^{2+}. This ion has an s^2p^1 electron configuration and is therefore bound to have a paramagnetic ground state irrespective of the ligand-field symmetry.

Russian scientists report ESR signals from both dilute hydrochloric acid solutions of $BiCl_3$ exposed to γ-radiation[2] and solutions of Bi and $BiCl_3$ in a (K,Li)Cl eutecticum.[13] However, the ESR spectra were recorded in the solid state and are thus not directly comparable to ours. The ESR lines found in those investigations were assigned to Bi(II) and Bi(IV) in aqueous solution (consistent with other radiochemical work)[3] and to the exotic adduct Bi^0–$BiCl_3$ (presumed by the authors to be tetrahedral) in the molten salt solution. Exposing a dilute hydrochloric acid solution of $BiCl_3$ to γ-radiation at room temperature was reported to produce a red solution of limited stability with the same visible spectroscopic properties as the one in this work, and without any detectable ESR signals.[2]

Optical spectroscopy. A solution of $BiCl_3$ in HCl(aq) is optically transparent at wavelengths > 420 nm, whereas the Bi(III)–Cl charge-transfer absorption makes measurements below this limit impossible.

The reduced solutions at room temperature have a single band at 516 nm as the only prominent feature. This band shifts slightly to longer wavelengths with increasing temperature, and reaches 520 nm at 100°C (Fig. 1).

The quenching to room temperature of a solution equilibrated with metal at 200°C produces a brown solution with high background absorption and two poorly
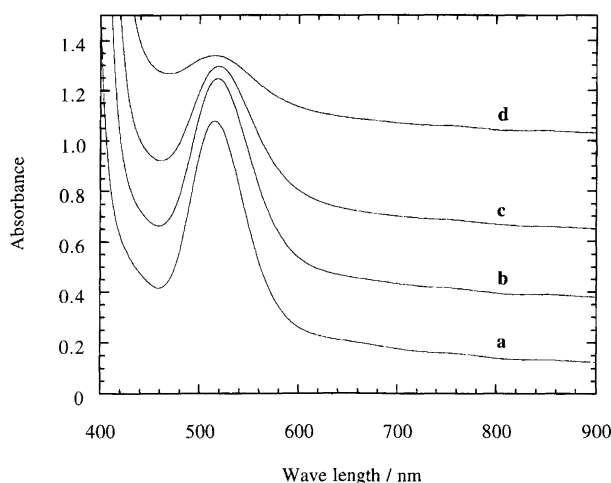

Fig. 1. Optical absorption spectra for [Bi–BiCl₃–HCl](aq) solutions saturated in Bi and $BiCl_3$ at (a) 25, (b) 50, (c) 75 and (d) 100°C. An empty sample cell was used as reference. The spectra have been vertically displaced for sake of clarity and normalized to an optical path length of 1.00 cm.
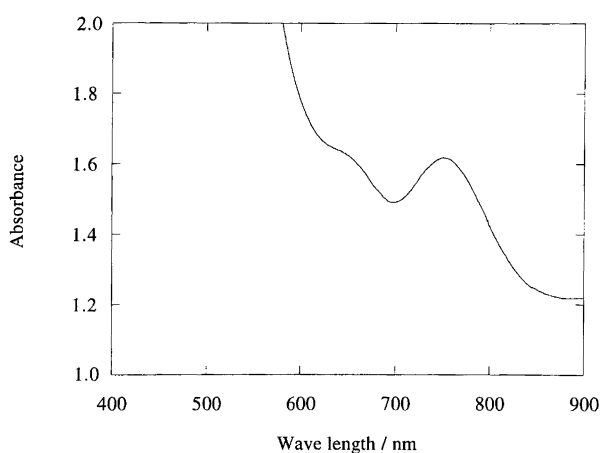
Fig. 2. Optical absorption spectra for a [BiCl₃–HCl](aq) solution saturated in BiCl₃ heated to 200°C in the presence of bismuth metal and then quenched to room temperature.

Fig. 3. The experimentally recorded absorption band and its Gaussian components as exemplified by the spectra at (A) 25 and (B) 100°C. The spectra have been corrected for the contribution from the Bi(III)—Cl charge-transfer absorption edge and normalized to an optical path length of 1.00 cm. The sum of the Gaussian components has been left out, since it coincides almost perfectly with the experimental curve.

defined bands at about 630 and 751 nm (Fig. 2). From such solutions, a black precipitate slowly forms and the red colour reappears. The precipitate gave metallic reflection of the laser radiation in an attempt to record a Raman spectrum and is therefore assumed to consist of metallic bismuth formed by the disproportionation of a subvalent species upon cooling. The brown colour and the two bands in the visible spectrum may be attributed to colloidal bismuth metal. Bi(0) centers in KCl have been shown to absorb at 629 and 725 nm,[14] which lends further support to this assumption. Furthermore, these two bands have also been detected for an (unknown) reduced bismuth species produced by the anodization of bismuth metal in a room-temperature molten salt system.[15]

The single absorption band in Fig. 1 can not be described by a single Gaussian line. A separation of the band into Gaussian components using the program LABCALC[16] reveals that the band shape can be accurately described by a sum of two Gaussian peaks (Fig. 3). The changes of the two component bands with temperature are displayed in Table 1. Since the ratio of the areas of the two components stays constant between 25 and 100°C, there is no obvious reason to assume that the component bands emanate from two light-absorbing species in equilibrium. Instead, we suggest that the experimentally found single band is due to two transitions in univalent bismuth, Bi⁺. This assignment rests on the close resemblance of the spectra to those obtained in Bi–BiX₃ (X = Cl, Br) solutions at higher temperatures.[17–19] Those spectral features have been interpreted as due to an equilibrium between two light-absorbing species, the one dominating at lower bismuth metal concentrations being assigned to Bi⁺ in accordance with data from EMF, vapour pressure and freezing point depression measurements.[19,20] The increase in wavelength of the absorption maximum for both component bands of the concentrated aqueous solution upon raising the temperature is also roughly consistent with the position of the
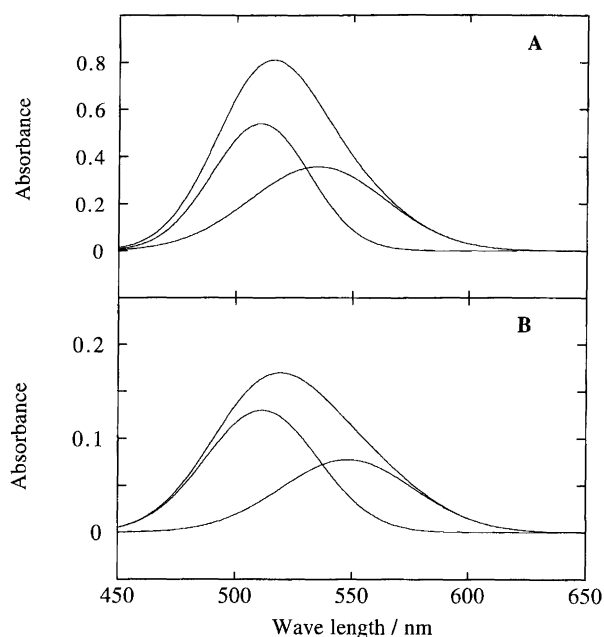
absorption maximum in the Bi–BiCl₃ solutions (560 nm) and in Bi–BiCl₃–(K,Li)Cl melts (552 nm).[13] The possibility that the reduced species is Bi²⁺ can be ruled out from the ESR measurements (*vide supra*). The ESR results also rule out the hypothetical inter-valence excitation Bi(I) + Bi(III)→2 Bi(II). The formation of condensed cationic species (i.e. clusters) seems highly improbable considering the low formal concentration of bismuth metal in the solutions, as well as previous reports which reveal that the formation of such species in molten salt media only is appreciable at much higher formal concentrations of metal than the ones in this study.[21,22] In molten salt solutions, based on the Lewis acids AlCl₃, AlBr₃ and ZnCl₂, the spectra of Bi⁺ have been shown to consist of several (≥4) bands in the visible region.[21,23] These spectra have been very well rationalized as emanating from p–p transitions in a ligand field of a symmetry lower than cubic.[24] However, the ground state of Bi⁺ was claimed to be ³P₂ or ³P₁ (depending on the ligand-field strength), with the lowest singlet state (¹D₂) some 30000 cm⁻¹ higher in energy. If this state of affairs was applicable to the present case, ESR lines from the triplet ground state (whether ³P₂ or ³P₁) would most likely be detectable. In view of the different spectral characteristics of Bi⁺ in different media, our suggestion is therefore that Bi⁺ represents the first example of a p–p system showing a ligand-field induced high-spin/low-spin duality (as far as this concept is applicable to systems with substantial

Table 1. Data from optical spectroscopy on the [Bi–BiCl₃–HCl](aq) system (saturated in Bi and BiCl₃) at various temperatures and from the deconvolution of the absorption band into two Gaussian components (denoted by subscripts 1 and 2). The errors, as obtained from the curve-fit, are one standard error. The data have been normalized to an optical path length of 1.00 cm.

$t/°C$	λ/nm	A	λ_1/nm	λ_2/nm	A_1	A_2	$Area_1/Area_2$
25	515.9	0.813	510.2	534.8	0.539±0.063	0.358±0.075	1.07±0.23
50	519.2	0.714	512.9	541.6	0.498±0.070	0.319±0.083	1.11±0.36
75	520.3	0.498	514.5	543.8	0.345±0.038	0.214±0.046	1.14±0.24
100	519.8	0.168	511.8	549.4	0.135±0.018	0.0739±0.019	1.40±0.29

spin–orbit coupling) and that in molten BiCl₃ as well as in the present system it adopts the latter electronic state.

It must be pointed out that the data presented here are not extensive enough to rule out an equilibrium between Bi⁺ and another (diamagnetic) species with absorption maxima ≤420 nm in the UV/VIS spectra. The fact that a disproportionation of some kind takes place when solutions heated to 200°C are cooled to room temperature indicates the presence of a second species stable at higher temperatures, since the stability of Bi⁺ is clearly decreased by increasing temperature. An investigation of such an equilibrium would require a careful study of the relation between the absorptivity and formal concentration of dissolved bismuth metal. Such a study is strongly disencouraged by the low solubility of bismuth metal and extreme sensitivity of the reduced solutions towards oxidation.

It should be noted that other reducing agents have the potential to bring about an identical reduction of Bi³⁺. An attempt to use Pb(s) as a reducing agent in the present investigation initially produced a scarlet solution with the same spectral characteristics as those in which Bi(s) was used. This is analogous to Pb–BiCl₃ melts which show the same spectral characteristics as Bi–BiCl₃ systems.[25] However, the solutions with Pb(s) present are unstable, and the reduction goes further, producing a colourless solution with Bi(s) and a white precipitate (presumably PbCl₂) as final products.

Raman spectroscopy. In order to obtain information about the nature of the chlorobismuthate(III) complex dominating in the saturated BiCl₃–HCl(aq) solution, the Raman spectrum of the system was recorded. The spectrum (Fig. 4) shows the characteristics of the previously reported spectra of BiCl₄⁻ in the solid state and in aqueous solution.[26] The position of the most intense band at 297 cm⁻¹ is very close to the position of the totally symmetric mode in BiCl₄⁻ in dilute aqueous solution (293 cm⁻¹) and in the solid state (290 cm⁻¹).[26] Although an unambigious band separation proved to be impossible to obtain, the shoulder on the low-frequency side of the 293 cm⁻¹ peak presumably contains contributions from the less intense BiCl₄⁻ peaks at 267 and 220 cm⁻¹ reported in the solid state, as well as minor contributions from other $BiCl_n^{3-n}$ ($n \neq 4$) complexes present in lower concentrations. The assumption that BiCl₄⁻ is the dominating chlorobismuthate species is therefore in agreement both with Raman spectra and with what should be ex-

pected from the formal composition of the solution (approximately HBiCl₄·3H₂O).

As would be expected from the low concentration of the reduced bismuth species at room temperature, the change in the low-frequency part of the Raman spectrum upon dissolution of the metal is very small, only amounting to a minor shift of 4 cm⁻¹ to higher frequency in the position of the most intense band (Fig. 4). The same shift is also found for the brown sample obtained by quenching a saturated solution from 200°C to room temperature, as described above. A tentative explanation for this shift, which is consistent with the formation of Bi⁺ discussed above, is that a chloro complex of Bi⁺ is formed, for which the Raman frequencies ought to be slightly different from those of the dominating chloro complexes of Bi³⁺. Such an explanation is also consistent with claims that Bi⁺ indeed has the ability to form covalent complexes.[21] However, the concentration of chloride ions for Bi⁺ complex formation in the present study has to be considered as being exceedingly low. The Bi/Cl ratio is slightly less than 4, and therefore a portion of the Bi³⁺ ions must be coordinatively unsaturated (strongly Lewis-acidic $BiCl_n^{3-n}$ complexes with $n \leq 3$). In fact, the acidity of the solvent may be of vital importance for the stability
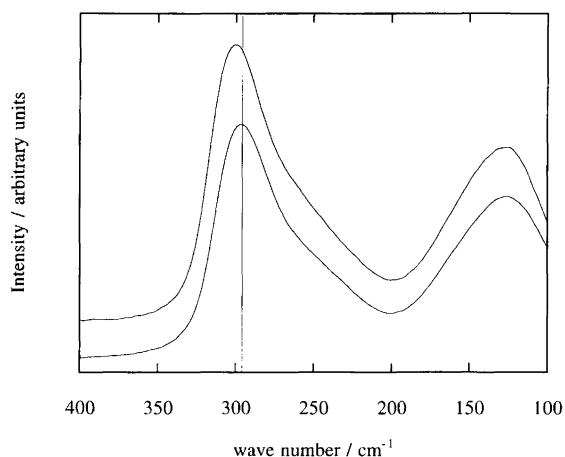

Fig. 4. Room-temperature Raman spectra of a saturated solution of BiCl₃ in aqueous hydrochloride acid (bottom) and the same solution reduced by bismuth metal at room temperature (top). The position of the band maximum at 297 cm⁻¹ for the former solution is marked by a vertical line in order to show the small (4 cm⁻¹) shift of the band upon dissolution of bismuth.

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of the Bi^+ ion, as has previously been discussed in connection with other subvalent main-group metal species and rationalized in terms of 'acid-stabilization' or 'anti-coordination chemistry'.[7] Keeping this in mind, a chemically more reasonable explanation for the observed frequency shift is a coordination of tetrachlorobismuthate(III) ions by the (presumably) less acidic Bi^+ ion, and a concommitant shift of the bands belonging to the former.

Our conclusion is that the univalent bismuth ion Bi^+ is stable at concentrations ≤ 6.4 mM in saturated aqueous hydrochloric acid solutions of $BiCl_3$, giving a molar extinction coefficient of 1.3×10^2 cm^{-1} M^{-1} for Bi^+. In contrast to $AlCl_3$- and $ZnCl_2$-based solvent systems this ion, presumably coordinated to $BiCl_4^-$ ions, may have a singlet ground state in this medium as is indicated from the lack of signals in the ESR measurements. It is thus possible that Bi^+ provides us with an example of a ligand-field induced low-spin/high-spin situation for an ion with p–p electronic transitions as well as being the first subvalent post-transition metal ion shown to be stable in aqueous solution.

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