Synthesis of Main-group Metal Clusters in Organic Solvents

Stefan Ulvenlund, Andrew Wheatley and Lars A. Bengtsson*

Inorganic Chemistry 1, University of Lund, Chemical Center, PO Box 124, S-221 00 Lund, Sweden

Oxidation of bismuth metal by Ga^{III} in $GaCl_3$–benzene solution produces the subvalent species Bi^+ and Bi_5^{3+}, which are characterized by liquid X-ray scattering, Raman and UV–VIS spectroscopy.

In two recent publications we reported the results from detailed investigations of arene solutions of gallium(III) and gallium(I) chlorides.[1] In these investigations it was shown that Ga^{III} readily oxidizes gallium metal to Ga^{I} in benzene solution. This opens the possibility of oxidizing also other main-group metals to subvalent species (clusters) in $GaCl_3$–benzene solutions. In this communication the reaction between bismuth and such solutions is reported. Bismuth was chosen as the cluster-forming element because of the comparatively large amount of spectroscopic data on bismuth cluster cations accumulated in the literature.

Subvalent main-group metal clusters have traditionally been synthesized either *via* high-temperature routes using molten salt solvents[2] or at room-temperature or lower by using so-called superacid solvents.[3] The fact that the reactivity of main-group metal clusters and the synthetic chemistry using such species as starting material remain almost completely unexplored, as compared to transition-metal cluster chemistry, may to a large extent be explained by the violent and indiscriminate reactivity of the solvents used so far. In order to expand our knowledge on such matters, it is thus highly desirable to find new routes to main-group metal clusters which utilize solvents of a less reactive nature. A step in this direction may be the use of organic solvents.

Because of the extreme moisture-sensitivity of anhydrous gallium(III) chloride all manipulations were performed in a glove box under dry nitrogen (< 0.5 ppm H_2O) using organic solvents distilled and stored over sodium. UV–VIS and Raman measurements were performed with the solutions enclosed in evacuated, flame-sealed 5 mm standard NMR tubes. Liquid X-ray scattering experiments were performed with the samples enclosed in sealed Lindemann capillaries as has previously been described in detail.[4] Between measurements, the samples were protected from light by a wrapping of aluminium foil in order to prevent photolysis.

Solvents consisting of gallium(III) chloride in aromatics (benzene or mesitylene) react with bismuth, yielding highly coloured solutions. However, the reaction is faster and more effective using benzene as solvent, presumably because of the stronger complex formation between $GaCl_3$ and mesitylene.[1] The UV–VIS spectra [Fig. 1(*a*)] identify the reaction products Bi^+ and Bi_5^{3+} which have been spectroscopically characterized.[5–7] The decreasing stability of the cluster cation with increasing temperatures, previously observed in the liquid Bi–$BiCl_3$–$AlCl_3$ system,[6] is evident also in the present system. The presence of two isosbestic points is noteworthy as a further indication that Bi^+ and Bi_5^{3+} are the only (light-absorbing) subvalent bismuth species present.

In the Raman spectra, an increase in the formal bismuth concentration produces an increase in the intensity of a strong band at 135 cm^{-1} corresponding to the A_1' mode in Bi_5^{3+}.[5] Concomitantly, a band at 367 cm^{-1} attributable[1] to the terminal $GaCl_3$ stretch in $Ga_2Cl_7^-$ or $Ga_3Cl_{10}^-$ is also found to increase in relative intensity. ^{71}Ga NMR (which has previously been shown to be an effective tool in discriminating between Ga^I and Ga^{III} in solution),[1,8] shows increasing intensity of the Ga^I signal with increasing formal bismuth concentration. On the basis of the conclusions about the Ga–$GaCl_3$–benzene system, these observations lead us to formulate the general cluster-forming reaction between Bi and $GaCl_3$ in benzene solution as given by eqn. (1).

$$10\ Bi + (9n + 3)\ GaCl_3 \rightarrow 2\ Bi_5^{3+} + 3\ Ga^+ + 9\ Ga_nCl_{3n+1}^-, \quad n = 2 \text{ or } 3 \qquad (1)$$

The saturation of $GaCl_3$–benzene solutions with bismuth metal produces two liquid phases. The upper phase is brown, whereas the lower phase is completely opaque. The UV–VIS spectrum of the upper phase from a system with a formal mole fraction $x(GaCl_3) = 0.10$ with respect to benzene is displayed in Fig. 1(*b*).

The reduced radial distribution function, obtained by liquid X-ray scattering, of the lower phase of a $GaCl_3$–benzene solution saturated with bismuth is very similar to that reported[9] for liquid '$BiAlCl_4$' [later shown to correspond to the stoichiometry $(Bi_5^{3+})(AlCl_4^-)_3$].[10] A large peak at 3.13 Å agrees well with the average bismuth–bismuth distances in the solid tetrachloroaluminates $(Bi_5^{3+})(AlCl_4^-)_3$ (3.12 Å),[10] and $(Bi_8^{2+})(AlCl_4^-)_2$ (3.10 Å),[11] as well as in $(Bi^+)(Bi_9^{5+})(HfCl_6^{2-})_3$[12] and $(Bi_9^{5+})_2(Bi_2Cl_8^{2-})(BiCl_5^{2-})_4$[13] (both 3.14 Å). Furthermore, a shoulder at 3.6 Å may be attributed to Bi···Cl correlations. The average Bi···Cl distance in $(Bi_5^{3+})(AlCl_4^-)_3$ is 3.65 Å. The interpretation of a peak at 6.29 Å and the question why the equatorial and axial Bi–Bi distances of Bi_5^{3+} not are resolved are currently under investigation. Reactions between $GaCl_3$–arene solvents and other main-group metals have also

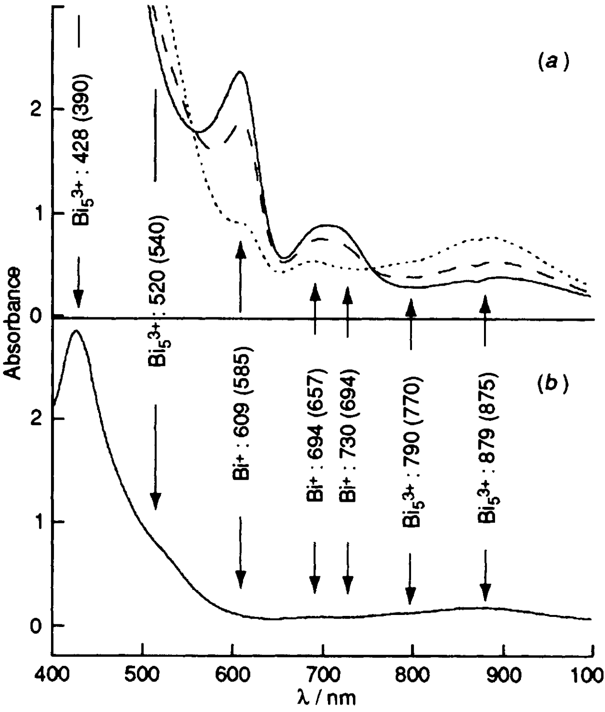

Fig. 1 (*a*) UV–VIS spectra of a solution of bismuth metal in a 30 mol% $GaCl_3$–benzene solution at different temperatures. The mole fraction of bismuth with respect to $GaCl_3$ is 0.0022. The spectrum recorded at 25 °C is displayed as a dotted line; at 50 °C as a dashed line and at 100 °C as a solid line. (*b*) UV–VIS spectrum at 25 °C of the upper phase of a 10 mol% $GaCl_3$–benzene solution saturated in bismuth metal. The numbers given are the band positions in nm. The positions of the corresponding bands in $AlCl_3$ media are taken from ref. 6 and given in brackets.

been observed. For instance, in the case of tellurium, the general appearence of the UV–VIS spectrum is in agreement with that previously reported for mixtures of Te^{2+} and Te_2^{2+} in $ZnCl_2$–KCl melts.[14] However, the solubility is much lower than for bismuth and no useful NMR or Raman data could be obtained.

The details of these intriguing systems will be the subject of forthcoming publications.

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References

1 S. Ulvenlund, A. Wheatley and L. A. Bengtsson, accepted for publication in *J. Chem. Soc., Dalton Trans.*

2 J. D. Corbett, *Prog. Inorg. Chem.*, 1976, **21**, 129.

3 R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 49.

4 S. Ulvenlund and L. A. Bengtsson, *J. Mol. Struct.*, 1994, **326**, 181.

5 R. C. Burns, R. J. Gillespie and W. C. Luk, *Inorg. Chem.*, 1978, **17**, 3596.

6 N. J. Bjerrum, C. R. Boston and G. P. Smith, *Inorg. Chem.*, 1967, **6**, 1162.

7 N. J. Bjerrum, H. L. Davis and G. P. Smith, *Inorg. Chem.*, 1967, **6**, 1603.

8 H. Schmidbaur, T. Zafiropoulos, W. Bublak, P. Burkert and F. H. Köhler, *Z. Naturforsch., Ser. A*, 1986, **41**, 315.

9 H. A. Levy, M. A. Bredig, M. D. Danford and P. A. Agron, *J. Phys. Chem.*, 1960, **64**, 1959.

10 B. Krebs, M. Mummert and C. Brendel, *J. Less-Common Met.*, 1986, **116**, 159.

11 B. Krebs, M. Hucke and C. Brendel, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 445.

12 R. M. Friedmann and J. D. Corbett, *Inorg. Chem.*, 1973, **12**, 1134.

13 R. M. Friedmann and J. D. Corbett, *Inorg. Chim. Acta*, 1973, **7**, 525.

14 N. J. Bjerrum, *Inorg. Chem.*, 1972, **11**, 2648.