

Novel Ionic Media for Liquid Lasers

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In a search for 3–5 μm lasing materials, crystals of AlBr_6Sb are isolated from a phosphorus tribromide–aluminium tribromide–antimony tribromide ($\text{PBr}_3\text{--AlBr}_3\text{--SbBr}_3$) solution: this solid contains infinite chains of alternating $[\text{SbBr}_2]^+$ cations and $[\text{AlBr}_4]^-$ anions, linked by weak coordinate bonds, and represents the first structure containing the dibromostibinium(III) cation.

Lanthanide-doped inorganic liquids of the type phosphorus(v) oxide trichloride–tin(IV) chloride ($\text{POCl}_3\text{--SnCl}_4$) and selenium oxide dichloride (SeOCl_2) were extensively researched in the 1970s¹ and the neodymium (Nd^{3+}) doped $\text{POCl}_3\text{--SnCl}_4$ system was demonstrated to be a good 1.06 μm lasing material.² However, the advent of the solid-state hosts (which do not suffer from the difficulties of inherent thermal expansion and high refractive index shifts with temperature experienced by liquids) resulted in research in this area being discontinued. Recently, we have revived this work in a quest for laser sources in the important 3–5 μm atmospheric window. Currently, wavelengths of 3–5 μm can only be generated with significant power by the inconvenient DF and CO gas lasers,³ and by a very small number of emission lines from solid-state lasers such as $\text{Er}^{3+}\text{--YLiF}_4$.⁴ We have demonstrated⁵ that a series of lanthanide halides dissolved in a number of inorganic liquids (which possess low vibrational energies and transparency in the far- and mid-IR) yield long non-radiative lifetimes for the lanthanide ion excited states. The widely researched POCl_3 and SeOCl_2 based solvent systems are unsuitable for this application, owing to the high vibrational frequency of the P=O and Se=O bonds, which quench the 3–5 μm fluorescence. It was found that the 0.17% praseodymium-doped $\text{PBr}_3\text{--AlBr}_3\text{--SbBr}_3$ (mol ratio 20 : 1 : 1) solution yielded exceptionally good results. A significant question as to the role of the aluminium(III) bromide and the antimony(III) bromide remained. The presence of both components was necessary to dissolve the PrBr_3 . We demonstrate here that the compound formed between these two halides is not the expected adduct $\text{AlBr}_3\text{--SbBr}_3$, which has been characterized by electron diffraction in the gas phase,⁶ but the salt $[\text{SbBr}_2][\text{AlBr}_4]$, which contains the first crystallographically characterized example of the dibromostibinium(III) cation.

Solutions of equimolar mixtures of aluminium(III) bromide and antimony(III) bromide in phosphorus(III) bromide [in the presence or absence of praseodymium(III) bromide] deposit, upon standing, colourless monoclinic crystals of a solid of empirical formula AlBr_6Sb . A compound of this composition

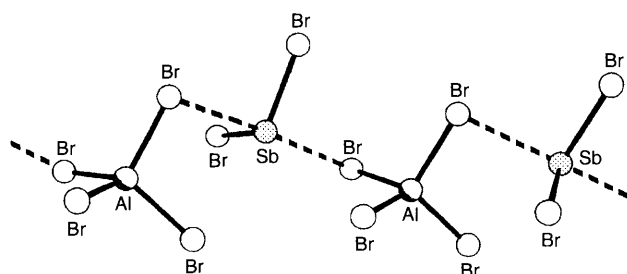


Fig. 1 $[\text{SbBr}_2][\text{AlBr}_4]$: Infinite chains of alternating anions and cations propagate through the structure: the bridging tetrabromoaluminate(III) anions are weakly coordinated to the dibromostibinium(III) cations. The terminal Sb–Br distances average at 0.2491 nm, with $\text{Br}_t\text{--Sb--Br}_t$ 96.7°, whereas the bridging bonds average at 0.2884 nm, with $\text{Br}_b\text{--Sb--Br}_b$ 175.6°. The terminal AlBr_t bonds average at 0.2259 nm, with $\text{Br}_t\text{--Al--Br}_t$ 116.8°, whilst the longer bridging bonds average at 0.2346 nm, with $\text{Br}_b\text{--Al--Br}_b$ 106.2°.

was first reported in 1923,⁷ where the phase diagram of the $\text{SbBr}_3\text{--AlBr}_3$ system showed unambiguous evidence for compound formation at the 50 mol% composition (mp 85.2 °C). In 1969,⁶ this compound was shown, by electron diffraction, to be a molecular adduct in the gas phase [with $r(\text{SbAl}) = 0.252(2)$ nm, $r(\text{AlBr}) = 0.230(2)$ nm, $r(\text{SbBr}) = 0.251(2)$ nm], with an empirical enthalpy of formation⁸ at 298 K from its component solid crystalline halides of -18.0 ± 2.5 kJ mol⁻¹ [eqn. (1)]:



A nuclear quadrupole resonance study⁹ suggested that although molecular in the gas phase, the compound was ionic, $[\text{SbBr}_2][\text{AlBr}_4]$, in the solid state, with weak bonds between the component ions forming discrete ion pairs, and that $\text{Br--Sb--Br} = 97.3^\circ$. However, as these authors⁹ also concluded that AlI_6Sb was isostructural with AlBr_6Sb , having the structure $[\text{SbI}_2][\text{AlI}_4]$, their conclusions are somewhat undermined by Pohl's crystal structure of AlI_6Sb ,¹⁰ which showed it to consist of covalently-bound tetranuclear $\text{Al}_2\text{I}_2\text{Sb}_2$ units.

Crystallographic analysis[†] revealed that the crystals of AlBr_6Sb contained chains (see Fig. 1) of alternating aluminium and antimony moieties. The material is best described as $[\text{SbBr}_2][\text{AlBr}_4]$, with the four-coordinate, distorted trigonal-bipyramidal, antimony-containing cations exhibiting a stereochemically active lone-pair of electrons, and being stabilized by weak coordination to the distorted tetrahedral aluminium complex. The terminal Sb–Br_t distances average at 0.2491 nm, with $\text{Br}_t\text{--Sb--Br}_t$ 96.7° (rather close to the value predicted by NQR⁹), whereas the bridging bonds average at 0.2884 nm, with $\text{Br}_b\text{--Sb--Br}_b$ 175.6°. The terminal AlBr_t bonds average at 0.2259 nm, with $\text{Br}_t\text{--Al--Br}_t$ 116.8°, whilst the longer bridging bonds average at 0.2346 nm, with $\text{Br}_b\text{--Al--Br}_b$ 106.2°. The structure is very similar to that deduced by Mamantov and coworkers,¹¹ by comparison with the known structure of $[\text{SbCl}_2][\text{GaCl}_4]$.¹²

It is known that the tetrachloroaluminate(III) anion ligates a wide range of transition metals, lanthanides and actinides, to produce highly soluble complexes of general type $[\text{M}(\text{AlCl}_4)_n]^{(n-3)-}$ in acidic room-temperature ionic liquids.^{13,14} Pending an EXAFS study, it is a reasonable assumption that the praseodymium is present in these novel ionic media as $[\text{Pr}(\text{AlBr}_4)_n]^{(n-3)-}$ complexes.

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Footnote

[†] Crystal data for $[\text{SbBr}_2][\text{AlBr}_4]$: AlBr_6Sb , $M = 628.19$, monoclinic, space group $P2_1/n$, $a = 10.170(2)$, $b = 10.416(2)$, $c = 10.218(2)$ Å, $\beta = 91.19(2)^\circ$, $U = 1082.2(4)$ Å³, $Z = 4$, $D_c = 3.856$ Mg m⁻³, $F(000) = 1096$, $\mu = 24.709$ mm⁻¹. Data were collected on a crystal (0.52 × 0.53 × 0.18 mm), cut from a large block, using a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-K α radiation. The crystal stability was monitored every 100 reflections and there were no significant variations ($\pm 1\%$). Cell parameters were obtained from 35 accurately centred reflections in the range 2θ 10–25°. The crystal was held at ca. 120 K in a cold nitrogen stream and ω -scans were employed for data collection.

Lorentz and polarisation corrections were applied. An empirical ψ -scan absorption correction was applied, transmission range 0.617–0.047. A total of 1349 reflections was measured for $5.58 < 2\theta < 45$ and 1291 unique reflections were used in the refinement. The structure was solved by direct methods and the atoms were refined with anisotropic thermal parameters. The final parameters were $wR2 = 0.1436$ and $R1 = 0.0620$ [for $wR2$ the function minimised is $\sum[w(F_o^2 - F_c^2)^2]$ for all F^2 and for $R1$ the function minimised is $\sum[|F_o| - |F_c|]/\sum|F_o|$ for $[I > 2\sigma(I)]$, $S = 1.102$, 73 parameters, $(\Delta/\sigma)_{\max} < 0.001$, $(\Delta\rho)_{\max,\min} = 1.195, -2.086 \text{ e } \text{Å}^{-3}$ where the function minimised was $\sum[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + g_2P]$ where $P = [(F_o^2, 0)_{\max} + 2|F_c|^2]/3$. The SHELXTL PC¹⁵ and SHELXL 93¹⁶ packages were used for data reduction and structure solution and refinement.

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