The NS_4^- Anion; the Blue Species Formed by Heptasulphur Imide in Basic Media

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Summary The blue species formed from heptasulphur imide, S_7NH, in basic media has been isolated as the tetra-n-butylammonium salt and characterised as the NS_4^- anion.

WE recently reported that elemental sulphur[1] or alkali polysulphides[2] dissolve in hexamethylphosphoramide (HMPA) to give blue solutions ($\lambda_{\max}$ 618 nm), attributed to the S_3^- radical anion.[2] This work led to an investigation of the well known blue species formed by sulphur imides *e.g.* S_7NH in basic media, previously assigned to neutral sulphur molecules $S_n (n = 2—4)$,[3] the S_7N^- ion,[4] or an open chain form of S_7N^-.[5,6] Here we identify it as the NS_4^- anion.

S_7NH dissolves in HMPA to give a blue solution characterised by a visible absorption band at 595 nm.† S_7NMe does not form the 595 nm species in HMPA, although traces of dimethylamine in the solvent cause the direct formation of S_3^-. Acid hydrolysis of freshly prepared blue solutions of S_7NH in HMPA regenerates S_7NH, suggesting a close relationship of the 595 nm species with the cyclo-S_7N^- ion. We confirmed that the blue species is anionic by an electrical transference experiment,[4] and that it is diamagnetic by the n.m.r. method.[7]

Addition of tetra-n-butylammonium hydroxide to a solution of S_7NH in diethyl ether at $-78°$ produced a yellow-green precipitate, *cf.* $K^+S_7N^-$,[6] $Na^+S_7N^-$,[8] $Hg(S_7N)$,[9] which solid turned purple-blue after 3 days at room temperature. Elemental analysis supported the composition $Bu^n_4N(S_7N)$, but an *X*-ray powder photograph revealed the presence of orthorhombic cyclo-S_8. Elemental sulphur was removed by Soxhlet extraction of the blue solid with hexane under a nitrogen atmosphere. Complete analysis of the blue-black residue showed it to be $Bu^n_4N(S_4N)$ and solutions in HMPA or THF had visible spectra identical to those of S_7NH in HMPA. Thus, solutions of S_7NH in HMPA involve the following equilibria:

$$S_7NH \rightleftharpoons H^+ + \underset{\text{(yellow)}}{\text{cyclo-}S_7N^-} \rightleftharpoons \underset{\text{(blue)}}{NS_4^-} + \tfrac{3}{8}S_8$$

which account for earlier observations on the alkylation of S_7N^-.[5,6]

The i.r. spectrum of $Bu^n_4N(S_4N)$ (DMF) showed bands at 900m, 610s, and 580s cm^{-1} in addition to bands attributed to the $Bu^n_4N^+$ cation and the solvent. In the solid state (Nujol) the latter band showed splitting, 582s and 575s

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† The 595 nm species is slowly converted into S_3^- if the solvent contains traces of dimethylamine.

cm^{-1}. The i.r. data do not allow a choice between straight chain, branched chain, or cyclic structures to be made for the S_4N^- anion. A cyclic structure with S–N single bonds is unlikely, however, in view of the high S–N stretching frequency.[10]‡

Thus, the NS_4^- anion is the first non-cyclic thio-anion of nitrogen to be characterised, and it is an important intermediate in the synthesis of sulphur imides.[11]

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‡ The i.r. spectrum of yellow $Hg(S_7N)_2$ (Nujol) showed bands at 795m, 768m, 745m, and 720m cm^{-1}.

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