

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

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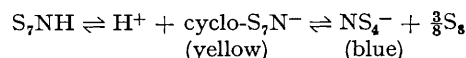
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Summary The blue species formed from heptasulphur imide, S_7NH , in basic media has been isolated as the tetra-*n*-butylammonium salt and characterised as the NS_4^- anion.

WE recently reported that elemental sulphur¹ or alkali polysulphides² dissolve in hexamethylphosphoramide (HMPA) to give blue solutions (λ_{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.* $\text{K}^+\text{S}_7\text{N}^-$,⁶ $\text{Na}^+\text{S}_7\text{N}^-$,⁸ $\text{Hg}(\text{S}_7\text{N})$,⁹ which solid turned purple-blue after 3 days at room temperature. Elemental analysis supported the composition $\text{Bu}_4\text{N}(\text{S}_7\text{N})$, 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 $\text{Bu}_4\text{N}(\text{S}_4\text{N})$ 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:



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

The i.r. spectrum of $\text{Bu}_4\text{N}(\text{S}_4\text{N})$ (DMF) showed bands at 900m, 610s, and 580s cm^{-1} in addition to bands attributed to the Bu_4N^+ cation and the solvent. In the solid state (Nujol) the latter band showed splitting, 582s and 575s

† 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 S₄N⁻ anion. A cyclic structure with S-N single bonds is unlikely, however, in view of the high S-N stretching frequency.^{10†}

Thus, the NS₄⁻ 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(S₇N)₂ (Nujol) showed bands at 795m, 768m, 745m, and 720m cm⁻¹.

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