Novel Route to Metallic Polythiazyl Bromides: Direct Bromination of S_4N_4

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Summary Metallic $(SNBr_{0\cdot25})_x$ may be readily prepared directly from S_4N_4 by the action of bromine followed by heating of the $(SNBr_{0\cdot4})_x$ which is first produced to 80 °C for 4 h.

AT present there is extensive interest in the synthesis and properties of metallic covalent polymers. Since the discovery of the metallic properties of polymeric sulphur nitride, $(SN)_x$, in 1973 by Walatka, Labes, and Perlstein,[1] many attempts to modify its properties or substitute other groups in the chain-like structure of $(SN)_x$ have been made.[2] Recently the first metallic derivative of $(SN)_x$, polythiazyl bromide $(SNBr_{0\cdot4})_x$, was reported independently by us as well as by Street *et al.*[3,4]

The synthesis of $(SN)_x$, from which $(SNBr_y)_x$ is made, involves the preparation of S_2N_2 (which is an unstable compound at room temperature and difficult to handle) and its polymerization. We now report a new synthesis of the metallic material directly from the bromination of S_4N_4.‡

In 1896 Clever and Muthmann described a material, $S_4N_4Br_4$, obtained by the bromination of S_4N_4 in CS_2 solution.[5] They also described a garnet red material, $S_4N_4Br_6$, obtained by reaction of bromine vapour with solid S_4N_4. Because of its insolubility in organic solvents and its deep bronze colour, Goehring considered that $S_4N_4Br_4$ was a linear polymer $[-S(Br)=N-]_x$.[6] Heal later reinvestigated the reaction of bromine with S_4N_4 in CS_2 solution and concluded that the bronze coloured material could be $S_3N_2Br_2$.[7]

We allowed 180 Torr of Br_2 vapour to react with powdered S_4N_4. Within 1 min the original orange colour of S_4N_4 changed to black to give a sticky material. Then, after some time, the original mass of S_4N_4 increased by swelling to give a free-flowing black powder. When weighed under 180 Torr of bromine vapour, the bromine content was as high as $(SNBr_{1\cdot5})_x$ after 16 h. When the $(SNBr_{1\cdot5})_x$ was pumped at room temperature for 4 h, a black powder of composition $(SNBr_{0\cdot4})_x$§ was obtained. The conductivity of compressed pellets of this material was *ca.* $3\cdot5 \times 10^2\ \Omega^{-1}\ cm^{-1}$ at room temperature. When $(SNBr_{0\cdot4})_x$ was heated with pumping at *ca.* 80 °C for 4 h, free bromine was liberated together with traces of S_4N_4 and a brown-black material. The residue had the composition $(SNBr_{0\cdot25})_x$§ and could readily be pressed into dark copper-coloured pellets.

X-Ray powder patterns of this material are almost identical with that of the copper-coloured crystals of $(SNBr_{0\cdot25})_x$ obtained by heating $(SNBr_{0\cdot4})_x$,[3,8] obtained from $(SN)_x$ and Br_2.

The conductivity of compressed pellets of $(SNBr_{0\cdot25})_x$ at 25 °C is *ca.* $1 \times 10^2\ \Omega^{-1}\ cm^{-1}$. This is in general agreement with what would be expected for a polycrystalline compaction based on the single-crystal data obtained from copper coloured $(SNBr_{0\cdot25})_x$ in directions parallel (*ca.* $2 \times 10^4\ \Omega^{-1}\ cm^{-1}$) and perpendicular (*ca.* $1 \times 10^1\ \Omega^{-1}\ cm^{-1}$) to the SN chain.[3] The conductivity is essentially temperature independent between room temperature and 4·2 K implying that the band gap is zero and that like the copper-coloured crystals of $(SNBr_{0\cdot25})_x$[3] prepared from $(SN)_x$ and Br_2, the material has metallic properties. It is interesting to note that the reaction reported in this communication involves the polymerization of the cradle-like cyclic S_4N_4 to SN chains in the product. This should provide a simple route for making other metallic derivatives of $(SN)_x$.

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‡ Street, *et al.* (*J.C.S. Chem. Comm.*, 1977, 464) have independently reported the preparation of $(SNBr_{0\cdot4})_x$ by bromination of S_4N_4 at 25 °C.

§ Satisfactory microanalytical data were obtained for this material.

[1] V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Letters*, 1973, **31**, 1139.
[2] See for example, C. Bernard, A. Herold, M. Lelaurain, and G. Robert, *Compt. rend.*, 1976, **283C**, 625.
[3] M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. J. Heeger, and D. L. Peebles, *J.C.S. Chem. Comm.*, 1977, 473; *Solid State Comm.*, 1977, **23**, 607.
[4] G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene, and J. J. Mayerle, *J.C.S. Chem. Comm.*, 1977, 407; W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Letters*, 1977, **38**, 1305.
[5] A. Clever and W. Muthmann, *Ber.*, 1896, **29**, 340.
[6] M. Goehring, *Quart. Rev.*, 1956, **10**, 437; 'Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen,' Akademie-Verlag, Berlin, 1957, p. 68.
[7] H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.
[8] M. Akhtar, C. K. Chiang, A. J. Heeger, J. Milliken, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, submitted for publication.