Synthesis and Structure of the Polymeric Metal, $(SN)_x$, and its Precursor, S_2N_2

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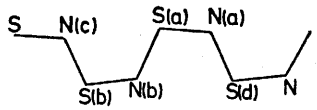
Summary The synthesis and *X*-ray structure of the polymeric metal, polymeric sulphur nitride, and the structure of S_2N_2, which undergoes polymerization in the solid state at room temperature to give $(SN)_x$, are described.

THE first synthesis of analytically pure‡ single crystals, suitable for solid-state studies, of the metallic[1-3] conductor, polymeric sulphur nitride, $(SN)_x$,[4] (polythiazyl), is reported. The $(SN)_x$ crystals were obtained by slowly growing crystals of S_2N_2 at 0° from the vapour phase during 48 h, followed by room temperature solid state polymerizaton over a period of *ca.* three days. Polymerization was completed by heating at 75 °C for 2 h. The initially colourless tabular monoclinic crystals of S_2N_2 turn dark blue at first and become paramagnetic ($g = 2{\cdot}005$) and then change to gold, diamagnetic crystals which are pseudomorphs of, and have the same space group ($P2_1/c$) as, the S_2N_2 crystals from which they are derived.

Scanning electron micrographs show the $(SN)_x$ crystals are composed of an ordered array of parallel $(SN)_x$ fibres.[2] The crystals are remarkable in that their room temperature conductivity (up to $2{\cdot}5 \times 10^3$ ohm^{-1} cm^{-1}) in a direction parallel to the fibres is comparable to that of a metal such as mercury. The temperature dependence of the conductivity is also characteristic of a metal, increasing *ca.* 25 times as the temperature is lowered to 10 K.[2]



Polythiazyl, $(SN)_x$, consists of an almost planar chain of alternating sulphur and nitrogen atoms. *Crystal data:*§ $a = 4{\cdot}153(6)$, $b = 4{\cdot}439(5)$, $c = 7{\cdot}637(12)$ Å; $\beta = 109{\cdot}7(1)°$ with $D_c = 2{\cdot}30$ g cm^{-3} for four SN units per unit cell. The refined structure ($R = 0{\cdot}11$) has as its major feature $(SN)_x$ chains with intrachain distances: S(a)–N(a) = 1·593(5), S(a)–N(b) = 1·628(7), S(a)–S(b) = 2·789(2), N(a)–N(b) = 2·576(7) and S(a)–N(c) = 2·864(5) Å and bond angles S–N–S = 119·9(4) and N–S–N = 106·2(2)°. These results are markedly different from those obtained in an earlier electron diffraction study.[5]

‡ A typical analysis of $(SN)_x$ was as follows: Calc.: S, 69·59; N, 30·41%. Found: S, 69·51; N, 30·56% (performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York 11377) and included specific analyses for carbon and hydrogen, both of which were found to be absent. Emission spectrographic analyses showed no measurable metal impurities (< 5 p.p.m.).

§ *X*-ray studies performed by Molecular Structure Corporation, College Station, Texas 77840.

In order to attempt to understand the solid state polymerization of S_2N_2 to $(SN)_x$ a single crystal *X*-ray structural study of S_2N_2 was performed at −130 °C. *Crystal data*:§ $a = 4{\cdot}485(2)$, $b = 3{\cdot}767(1)$, $c = 8{\cdot}452(3)$ Å; $\beta = 106{\cdot}43(3)°$ with $D_c = 2{\cdot}23$ g cm^{-3} with two S_2N_2 molecules per unit cell; $R = 0{\cdot}027$. The molecule is square planar with essentially equal S–N bond lengths [1·651(1) and 1·657(1) Å]. The S–N–S– angle is 90·42(6)° and the N–S–N angle is 89·58(6)°. Further details will be reported elsewhere.[2]

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[1] A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski, P. J. Russo, and A. G. MacDiarmid, *Phys. Rev. Letters*, 1975, **34**, 206.

[2] A. A. Bright, C. K. Chang, M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, and M. S. Saran, to be published.

[3] A. A. Bright, M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid and C. M. Mikulski, *Appl. Phys. Letters*, in the press; V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Letters*, 1973, **31**, 1139; C. Hsu and M. M. Labes, *J. Chem. Phys.*, 1974, **61**, 4640.

[4] See H. G. Heal, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 375.

[5] M. Boudeulle, Ph.D. Thesis, University Claude-Bernard De Lyon, 1974.