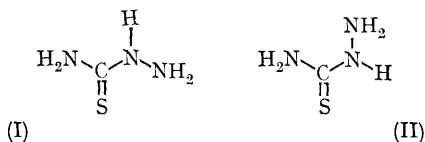


Trigonal Silver(I) and Polymer Chains of Co-ordination Polyhedra in catena- μ -Thiocyanato-bis(thiosemicarbazide)silver(I)

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THIOSEMICARBAZIDE can behave as a chelating agent with conformation (I)¹ or as a monodentate ligand with conformation (II). Monodentate



behaviour was found in polymeric monochloro-mono(thiosemicarbazide)silver² and now in catena- μ -thiocyanato-bis(thiosemicarbazide)silver in which polymer chains of co-ordination polyhedra are present.

Crystallographic data for catena- μ -thiocyanato-bis(thiosemicarbazide)silver, AgNCS[SC(NH₂)NH·NH₂]₂ are: $a = 11.44(1)$, $b = 14.96(3)$, $c = 6.57(1)$ Å, $Z = 4$, $D_m = 2.01$, $D_c = 2.06$ g.cm.⁻³, space group: $Pna2_1$ (from Weissenberg photographs, Cu- K_α). The crystal structure was determined by conventional Patterson and Fourier techniques and refined applying Booth's differential synthesis to the residual error index $R = 0.14$ for the 679 independent reflections observed on the $hk0 \dots hk5$ Weissenberg photographs.

The silver co-ordination polyhedron is rather unusual, being a distorted trigonal pyramid involving two sulphur atoms, S(1) and S(2), from two thiosemicarbazide molecules, and one nitrogen atom, N(7), and one sulphur atom, S(3), from two different NCS groups, as shown in the clinographic projection of the Figure. The NCS groups are in

bridging position between two silver atoms and link the co-ordination polyhedra in zig-zag chains, running parallel to [001]. However, the bonds

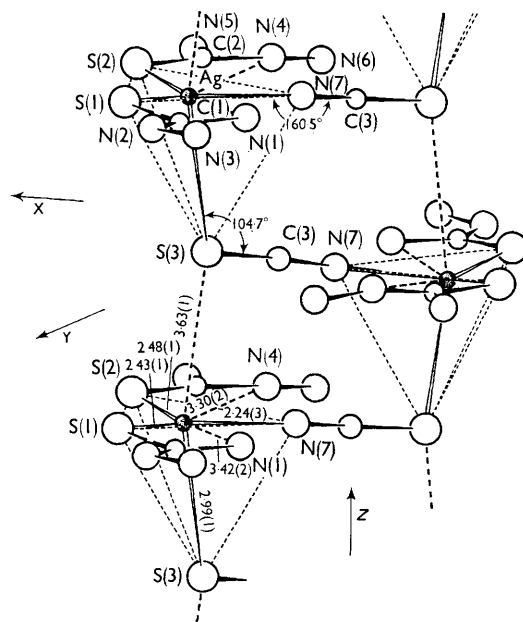


FIGURE. Clinographic projection of chains of co-ordination polyhedra in AgNCS[SC(NH₂)NH·NH₂]₂. Distances are in Å, the standard deviations given in parentheses.

formed by the two ends of the NCS group are not equal in strength, the bonding through sulphur

being much weaker as is indicated by the rather long Ag-S(3) distance (2.99 Å). This accounts for the i.r. spectrum of the compound in which the values of the frequencies for the symmetric ($\nu_3 = 2083 \text{ cm.}^{-1}$, C≡N stretching) and anti-symmetric ($\nu_1 = 790 \text{ cm.}^{-1}$, C-S stretching) vibrational modes of the NCS group, correspond to those generally found for the isothiocyanates when NCS

co-ordinates through nitrogen ($\nu_3 = 2080\text{--}2095 \text{ cm.}^{-1}$,³ $\nu_1 = 780\text{--}860 \text{ cm.}^{-1}$).^{4,5} The configuration of the shortest bonds formed by Ag is therefore sp^2 trigonal. Three longer contacts, $\text{Ag} \cdots \text{S}(3') = \text{Ag} \cdots \text{N}(1) = 3.42$ and $\text{Ag} \cdots \text{N}(4) = 3.30 \text{ \AA}$, complete the co-ordination polyhedron to a distorted pentagonal bipyramid.

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