

Configuration of Thiosemicarbazide Molecule in Monochloromonothiosemicarbazidesilver

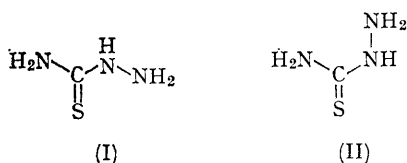
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CHEMICAL evidence¹ and *X*-ray structural determinations have shown that thiosemicarbazide behaves as a bidentate ligand with configuration (I) in dichloromonothiosemicarbazidezinc,² in

¹ K. A. Jensen and E. Rancke-Madsen, *Z. anorg. Chem.*, **1934**, **219**, 243; K. A. Jensen, *ibid.*, **1934**, **221**, 6, 11.

² L. Cavalca, M. Nardelli, and G. Branchi, *Acta Cryst.*, **1960**, **13**, 688.

bisthiosemicarbazidatonickel³ and in *trans*-bisthiosemicarbazidenickel sulphate trihydrate.⁴ Configuration (II) is observed for the first time in monochloromonothiosemicarbazidesilver in which thiosemicarbazide acts as a monodentate ligand being co-ordinated only through the sulphur atom. This behaviour is similar to that observed for biuret which can assume different configurations in various metal complexes.⁵

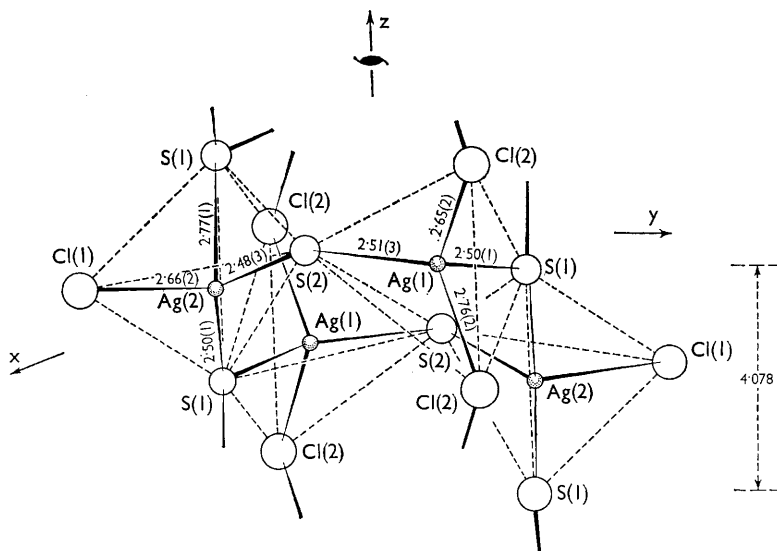


Monochloromonothiosemicarbazidesilver, $\text{Ag}[\text{SC}(\text{NH}_2)\text{NHNH}_2]\text{Cl}$, crystallizes in very slender colourless orthorhombic needles, elongated along [001]: $a = 11.9_3$, $b = 24.8_8$, $c = 4.07_8$ Å, $Z = 8$, $D_m = 2.69$ (by flotation), $D_c = 2.57$ g.cm.⁻³. Space group: $P 2_12_12_1$. A three-dimensional X-

ray structural analysis of the complex has been completed using conventional Patterson and Fourier techniques. The refinement, carried out with three isotropic and four anisotropic cycles of Booth's differential synthesis, has converged the R index to its present value of 11.0% for the 862 reflections observed on the $h\bar{k}0, \dots, h\bar{k}3$ Weissenberg photographs.

Two kinds of silver atoms are present both with a tetrahedral surrounding: Ag(1) co-ordinates two chlorine and two sulphur atoms, Ag(2) is bonded to one chlorine and to three sulphur atoms (see Figure). There are also two kinds of chlorine atoms, Cl(1) forming one and Cl(2) forming two co-ordinative bonds, and two kinds of sulphur atoms, S(1) co-ordinated to three and S(2) to two silver atoms respectively. This is another example of sulphur bridging.⁶ The complex is polymeric, the co-ordination polyhedra being linked in helical chains around a 2_1 axis parallel to the c direction in which a particularly short translation period is observed.

The same structure is present in monobromomonothiosemicarbazidesilver.



A chain of co-ordination polyhedra in $\text{Ag}[\text{SC}(\text{NH}_2)\text{NH}\cdot\text{NH}_2]\text{Cl}$. The axis of the chain is a 2_1 axis parallel to Z . Distances are in a Å, the standard deviations given in parentheses are in units of the second decimal place.

(Received, April 6th, 1965.)

³ L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, 1962, **15**, 1139.

⁴ R. Grønbaek and S. E. Rasmussen, *Acta Chem. Scand.*, 1962, **16**, 2325.

⁵ M. Nardelli, G. Fava, and G. Giraldi, *Acta Cryst.*, 1963, **16**, 343.

⁶ M. Nardelli, G. Fava, and P. Boldrini, *Gazzetta*, 1962, **92**, 1392.