



Doctoral Thesis

## **Etude de la structure cristalline du sel double $\text{Ag}_3(\text{SCN})(\text{NO}_3)_2$ et de ses propriétés physico-chimiques**

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**Thèse No 4243**

**ETUDE DE LA STRUCTURE CRISTALLINE DU SEL DOUBLE**  
 **$\text{Ag}_8(\text{SCN})(\text{NO}_3)_2$**   
**ET DE SES PROPRIETES PHYSICO-CHIMIQUES**

Thèse présentée à  
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Structure determination of the thiocyanate and dinitrate  
silver complex

-Summary-

The double salt  $\text{Ag}_3(\text{S C N})(\text{NO}_3)_2$  crystallizes in the space group  $\bar{P}1$  with two formula units in the elementary cell. The cell constants are as follows:

$$a=7.6 \text{ \AA} \quad , \quad b=7.9 \text{ \AA} \quad , \quad c=6.5 \text{ \AA} \quad , \quad \alpha=95^\circ \quad , \quad \beta=90^\circ \quad , \quad \gamma=104^\circ$$

In the unit cell there are 28 atoms, two of which occupy special positions:

$$\text{Ag}_I \quad a(\bar{1}) \quad 0,0,0 \quad \text{and} \quad \text{Ag}_{II} \quad b(\bar{1}) \quad 0,0,1/2$$

The other 26 atoms occupy the general positions:

Atoms	X	Y	Z	Atoms	X	Y	Z
2 $\text{Ag}_{III}$	.73 <sub>0</sub>	.36 <sub>2</sub>	.04 <sub>6</sub>	2 $\text{O}_V$	.53 <sub>8</sub>	.59 <sub>2</sub>	.23 <sub>6</sub>
2 $\text{Ag}_{IV}$	.35 <sub>7</sub>	.67 <sub>9</sub>	.47 <sub>5</sub>	2 $\text{O}_{VI}$	.79 <sub>7</sub>	.68 <sub>8</sub>	.08 <sub>4</sub>
2 S	.21 <sub>4</sub>	.89 <sub>8</sub>	.22 <sub>8</sub>	2 $\text{N}_I$	.05 <sub>6</sub>	.34 <sub>7</sub>	.35 <sub>1</sub>
2 $\text{O}_I$	.19 <sub>0</sub>	.36 <sub>2</sub>	.42 <sub>2</sub>	2 $\text{N}_{II}$	.69 <sub>6</sub>	.72 <sub>0</sub>	.14 <sub>0</sub>
2 $\text{O}_{II}$	.08 <sub>4</sub>	.51 <sub>4</sub>	.23 <sub>1</sub>	2 $\text{N}_{III}$	.51 <sub>4</sub>	.18 <sub>3</sub>	.25 <sub>7</sub>
2 $\text{O}_{III}$	.93 <sub>2</sub>	.22 <sub>7</sub>	.29 <sub>3</sub>	2 C	.39 <sub>2</sub>	.05 <sub>7</sub>	.24 <sub>0</sub>
2 $\text{O}_{IV}$	.67 <sub>7</sub>	.86 <sub>2</sub>	.27 <sub>4</sub>				

The intensities of 305 reflexions (Weissenberg  $\text{Cu } k_\alpha$ ) were estimated visually. As a result of calculation and refinement, assuming isotropic temperature factors, the reliability factor was found to be:

$$R = \frac{\sum \left| |F_o(hk1)| - |F_c(hk1)| \right|}{\sum |F_o(hk1)|} = .117$$

Figures (22), (23), and (24) show respectively the projections of the structure in the planes (XYO), (OYZ), and (XOZ). Figure (12) gives the appearance of part of the crystal lattice, seen by an observer viewing both sides of the horizontal plane (XY1/2); figure (13) is a simplified representation of the structure in the OZ-axis direction.

The chemical formula of the substance  $\text{Ag}_3(\text{SCN})(\text{NO}_3)_2$  corresponds to one polynuclear cation complex  $[\text{Ag}_3(\text{SCN})]^{++}$ , and two anions  $(\text{NO}_3)^-$ . The cations  $[\text{Ag}_3(\text{SCN})]^{++}$  are bound together in a tridimensional infinite network parallel to the plane (010). The figures (12) and (13) show the extension for the cations almost as layers. This is due to the weakly ionic nature of the silver.

The anions are discrete and distributed, as islands, so as to allow an equilibrium corresponding to a minimum energy in the crystalline lattice. The elementary cell contains four nitrate groups. Every two of these are centrosymmetric with the rest.

Within the limits of the experimental errors, it seems that:

- 1) Each S atom has four Ag atoms as near neighbours which form with the S atom, at the apex, the four points at the base of a distorted tetrahedron. The S-Ag distances are:  $\text{S-Ag}_I = 2.52 \text{ \AA}$ ,  $\text{S-Ag}_{II} = 2.61 \text{ \AA}$ ,  $\text{S-Ag}_{III} = 2.71 \text{ \AA}$ ,  $\text{S-Ag}_{IV} = 2.85 \text{ \AA}$ .
- 2) The atoms  $\text{Ag}_I$  and  $\text{Ag}_{II}$  both occupy centres of symmetry to give a zigzag chain  $\dots\text{S-Ag}_I\text{-S-Ag}_{II}\text{-S}\dots$  which extends along the OZ-axis. The angle  $\text{Ag}_I \text{ S } \text{Ag}_{II}$  is  $78^\circ$ .
- 3) Each N atom of the rhodanide group forms a triangle with  $\text{Ag}_{III}$  and  $\text{Ag}_{IV}$  atoms, where the angle  $\text{Ag}_{III} \text{ N } \text{Ag}_{IV}$  is  $91^\circ$ , and the distances:  $\text{N - Ag}_{III} = 2.40 \text{ \AA}$ ,  $\text{N - Ag}_{IV} = 2.08 \text{ \AA}$ . All other N - Ag distances are greater.
- 4) The chain  $\dots\text{Ag-S-C-N-Ag}\dots$  is not linear. It has the stereochemical trans form. There is an angle of  $103^\circ$  with S atom, and an angle of  $129^\circ$  with N atom. The interatomic distances  $\text{S-C} = 1.60 \text{ \AA}$  and  $\text{C-N} = 1.18 \text{ \AA}$  show these bonds essentially to be covalent.

5) The angle S-C-N is approximately  $175^\circ$ . This value is of the same order of magnitude as those reported in the literature for substances having the same rhodanide complexes. Moreover, the Walsh theory establishes the linearity of the SCN group, and of all anions of the type XYZ having 16 electrons.

Considering the experimental errors in the structure determination, we are inclined to accept the linearity of the rhodanide group.

6) The S atom is surrounded by an excess of Ag atoms whose repulsion apparently ensures that the SCN line is not in the  $Ag_I S Ag_{II}$  plane, but the SCN line appears to be in the  $Ag_{III} N Ag_{IV}$  plane.

7) The S atom appears to show a stronger attraction towards  $Ag_I$  than  $Ag_{II}$ . The N atom also exhibits a stronger attraction towards  $Ag_{IV}$  than  $Ag_{III}$ .

8) In the  $(NO_3)^-$  group, the bonds N-O are essentially covalent. The average value obtained for the interatomic distances N-O is  $1.28 \overset{\circ}{\text{Å}}$ , and the angle O-O-O has an average value of  $\sim 60^\circ$ .

9) According to the valence-bond theory, and considering the distribution of the electrons, the  $(NO_3)^-$  groups are believed to be planar, especially in the gaseous state or in the ionic compounds. This planarity is virtually verified here.

10) The triangles  $(NO_3)^-$  should be equilateral. The observed perturbations in the trigonal symmetry of this triangles together with the difference between the length N-O obtained and that reported in the literature ( $1.22 \overset{\circ}{\text{Å}}$ ), seem to bear no stereochemical significance. They do not seem to be caused by the influence of the Ag atoms, which are at least  $4 \overset{\circ}{\text{Å}}$  from the O atoms of the nitrate ions.

They are thus essentially due to the experimental errors in this structure determination.