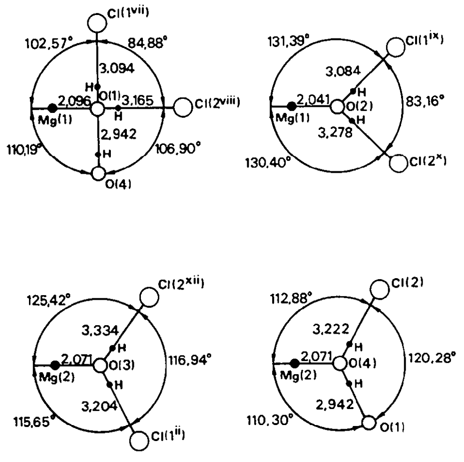

Fig. 2. Coordination des molécules d'eau avec positions probables des atomes d'hydrogène.

coordination des molécules d'eau est représentée schématiquement sur la Fig. 2.

Chaque octaèdre $Mg(1)(H_2O)_6$ établit des liaisons avec des octaèdres $CdCl_6$ centrés sur le même axe ternaire que lui et aussi avec des octaèdres $CdCl_6$ dont l'atome de cadmium a une cote voisine de celle de Mg(1) consideré; il est également lié à trois $Mg(2)(H_2O)_6$. Les octaèdres $Mg(2)(H_2O)_6$, empilés suivant un axe ternaire ne sont pas liés entre eux. Ils sont liés à six $CdCl_6$ et trois $Mg(1)(H_2O)_6$. Les octaèdres $CdCl_6$ sont uniquement liés aux groupements $Mg(1)(H_2O)_6$ et $Mg(2)(H_2O)_6$.

Tableau 3. *Distances* O—O *et* O—Cl *inférieures à* 3,5 Å

Code des notations: *cf.* Tableau 2. Seules sont indiquées les distances O—O entre oxygènes coordinés à des Mg différents (Baur, 1972). Les distances soulignées correspondent aux liaisons hydrogène réalisées par les H liés à l'oxygène cité en tête.

O(1)—O(4)	2,942 (6) Å	O(3)—Cl(1^{ii})	3,204 (4) Å
O(1)—Cl(1^{vii})	3,094 (4)	O(3)—O(1^{v})	3,324 (6)
O(1)—Cl(2^{viii})	3,165 (4)	O(3)—Cl(2^{xii})	3,334 (4)
O(1)—O(3^{vi})	3,324 (6)	O(3)—O(4^{viii})	3,451 (6)
O(2)—Cl(1^{ix})	3,084 (4)	O(4)—O(1)	2,942 (6)
O(2)—Cl(2^{x})	3,278 (5)	O(4)—Cl(2)	3,222 (5)
O(2)—O(4^{iv})	3,398 (6)	O(4)—O(2^{iii})	3,398 (6)
O(2)—Cl(1^{xi})	3,439 (4)	O(4)—O(3^{viii})	3,451 (6)
		O(4)—Cl(1^{ii})	3,497 (4)

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Structure of Trisilver(I) Sulfamide–Ammonia–Water at 108 K

By Christoph Kratky

Institut für Physikalische Chemie, Universität Graz, A-8010 Graz, Austria

and Edgar Nachbaur and Alois Popitsch

Institut für Anorganische und Analytische Chemie, Universität Graz, A-8010 Graz, Austria

(*Received* 6 *October* 1980; *accepted* 15 *December* 1980)

Abstract. $Ag_3(HN_2O_2S).NH_3.H_2O$, orthorhombic, *Pcam*, $a = 11{\cdot}813\ (6)$, $b = 9{\cdot}665\ (5)$, $c = 6{\cdot}578\ (2)$ Å (at 108 K), $Z = 4$, $d_x = 4{\cdot}01$ Mg m^{-3}, $R = 0{\cdot}06$ (1076 reflections, 40 parameters). The structure consists of alternating layers of Ag atoms and hydrogen-bonded NH_3, H_2O and sulfamide molecules. A possible connection between the observed anisotropic photoconductivity and the layer structure is discussed. The two sulfamide N atoms are covalently bonded to two and three Ag atoms.

Introduction. Crystals of the title compound are yellow, diamagnetic (Haselmair, 1979) and show anisotropic photoconductivity (Gruber, 1981). Both in color and in Ag content, they can be regarded as intermediate between the colorless disilver sulfamide Ag_2SA

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(Greschonig, Nachbaur & Krischner, 1977) and the deep-red Ag_4SA (Kratky & Popitsch, 1980). The preparation of $Ag_3SA.NH_3.H_2O$ was described previously (Nachbaur & Popitsch, 1973; formulated incorrectly as the ammonium salt); for the present work, however, a slightly modified synthesis was employed: silver nitrate and sulfamide (3:1) were suspended in dimethylformamide and dissolved by addition of 2*M* ammonia. After addition of an equimolar amount of potassium hydrogencarbonate, the solution was allowed to stand for several days in a desiccator (H_2SO_4), whereupon yellow crystals appeared. They darken after prolonged exposure to light.

Crystals grow in the form of very thin plates, with *b* perpendicular to the plane of the plate. The crystal used for the structure determination was mounted with *b* coincident with the goniometer-head axis. A set of precession photographs at room temperature established the two possible space groups compatible with the observed extinctions ($0kl$: $l = 2n$; $h0l$: $h = 2n$), $Pca2_1$ or *Pcam*. Cell dimensions were obtained by least squares from the setting angles of ten reflections determined at 108 K (recorded temperature) on a Stoe four-circle diffractometer equipped with a modified Nonius low-temperature device. Intensities (also measured at 108 K) were collected in the ω-scan mode with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). All reflections in one octant of reciprocal space with $2\theta < 60°$ ($\sin\theta/\lambda \leq 0{\cdot}704$ Å^{-1}) were recorded, yielding 1191 reflections (including 115 systematically extinct).

Data reduction [872 reflections with $|F_o| > 3\sigma(|F_o|)$] involved the Lp correction but, at that point, no absorption correction, because of the impossibility of measuring the thickness of the crystal (μ = 7·7 mm^{-1}). The structure was solved with a combination of direct methods (*MULTAN* 77, Germain, Main & Woolfson, 1970) and difference syntheses in $Pca2_1$. Isotropic refinement in the same space group converged at a centrosymmetric structure (R = 0·16), although the refinement had been started with a non-centrosymmetric trial structure. The space group was therefore changed to *Pcam*.

The rather high *R* was mainly attributed to the neglect of absorption errors. Since, for the particular mounting of the crystal (*b* parallel to the diffractometer φ axis), the absorption correction is, to a first approximation, a function of *k* only, the refinement (in *Pcam*) was continued with a separate scale factor for each layer with a different *k*. With 13 scale factors and isotropic temperature factors for all non-hydrogen atoms, the refinement converged at R = 0·06 {weighting scheme: $A/[\sigma^2(F) + BF_o^2]$, A = 0·79, B = 0·0041; Sheldrick (1976)}. No attempt was made to refine the anisotropic temperature factors in view of the expected correlation with the interlayer scale factors. H atoms could not be observed and were not included in the refinement. Since N could not be distinguished from O on the basis of the crystallographic evidence alone (Kratky & Popitsch, 1980), the assignment of N and O was made according to chemical plausibility. [Computer programs used: XRAY (Stewart, 1976) and *SHELX* (Sheldrick, 1976).]

Table 1. *Fractional atomic coordinates and U values* ($\times 10^4$, *U in* Å^2) *for trisilver*(I) *sulfamide*

The temperature factor has the form
$T = \exp[-(8\pi^2 U \sin^2\theta/\lambda^2)]$.

	x	*y*	*z*	*U*
Ag(1)	2362 (1)	2299 (1)	2500	111 (3)
Ag(2)	−1220 (1)	5199 (1)	4958 (1)	103 (3)
S	−227 (2)	2681 (3)	2500	94 (5)
N(1)	912 (8)	3571 (9)	2500	102 (17)
N(2)	−1299 (8)	3799 (9)	2500	97 (17)
O	−320 (5)	1858 (6)	4325 (11)	155 (11)
$N(NH_3)$	−1289 (9)	−908 (10)	2500	148 (20)
$O(H_2O)$	−3065 (8)	1728 (10)	2500	188 (18)

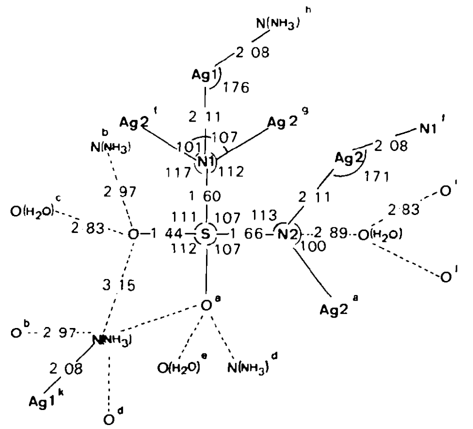

Fig. 1. Bonding geometry in the trisilver(I) sulfamide crystal structure. Dashed lines indicate assumed hydrogen bonds. (*a*) $x, y, \frac{1}{2} - z$; (*b*) $-x, -y, 1 - z$; (*c*) $-\frac{1}{2} - x, y, \frac{1}{2} + z$; (*d*) $-x, -y, -\frac{1}{2} + z$; (*e*) $\frac{1}{2} - x, y, -z$; (*f*) $-x, 1 - y, 1 - z$; (*g*) $-x, 1 - y, -\frac{1}{2} + z$; (*h*) $\frac{1}{2} + x, -y, \frac{1}{2} - z$; (*i*) $-\frac{1}{2} - x, y, -\frac{1}{2} + z$; (*j*) $-\frac{1}{2} - x, y, 1 - z$; (*k*) $-\frac{1}{2} + x, -y, \frac{1}{2} - z$. Standard deviations: bond lengths and contact distances: 0·01 Å; bond angles: 0·5°.

Atomic coordinates are given in Table 1.* Bond distances and angles are shown in Fig. 1.

Discussion. The Ag atoms are arranged in layers parallel to the *xz* plane; along *y*, these layers alternate with layers of hydrogen-bonded solvent molecules. The N atoms of the sulfamide molecules face the Ag layers, while the sulfamide O atoms are involved in the hydrogen-bonding network (Figs. 2 and 3).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35778 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

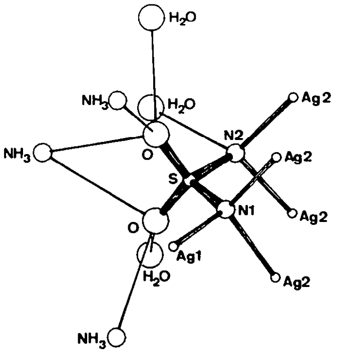

Fig. 2. ORTEP (Johnson, 1965) drawing of one sulfamide molecule with its directly-coordinated neighbors.

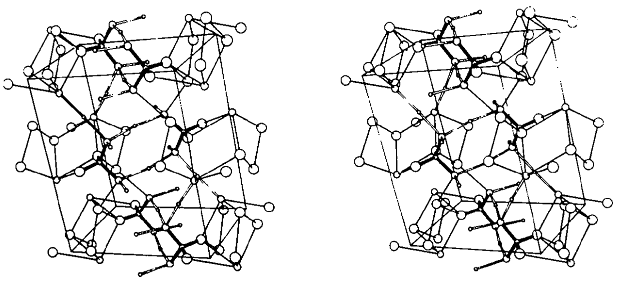

Fig. 3. Stereopicture of the crystal structure of Ag_3SA. The x axis runs upwards, y from left to right and z into the plane of the paper.

Within the layers of Ag atoms, chains of Ag(2) atoms with 2·91 and 3·02 Å separation run along x. Along z, the Ag(2)···Ag(2) contacts are 3·23 and 3·34 Å. This arrangement of Ag atoms could give an explanation for the anisotropy in the photoconductivity: for the conductivity along x, the action spectrum has its maximum at lower energy (~430 nm) than along z (~375 nm). So far, no conductivity measurements could be carried out along y, but the structure would support the prediction that the photoconductivity along y should require far higher energies than along x or z.

The linear, twofold coordination of N around the Ag atoms (Fig. 1) is as expected for covalent Ag. The coordination of Ag atoms around sulfamide N shows an increase in observed coordination numbers from Ag_2SA to Ag_3SA and Ag_4SA: coordination numbers for SA N atoms are 2 and 2 in the white Ag_2SA, 2 and 3 in the yellow Ag_3SA and 3 and 4 in the red Ag_4SA, respectively. A possible correlation of this coordination number with the color is supported by several other structurally known Ag^I compounds.

CK acknowledges support from the Österreichischer Fonds zur Förderung der wissenschaftlichen Forschung (Projekt No. 3763) and the Österreichische Akademie der Wissenschaften.

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