which differ only in sign. The positive set was chosen: $D_{K(+)} = 143.41$; $D_{Br(-)} = 55.31$. These values, however, could have been merely arbitrarily chosen because only the difference in the *D* parameters is used in calculating the dissociation energies.

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Crystal Structure of 2-Sulfanilamidopyrimidinesilver(I)

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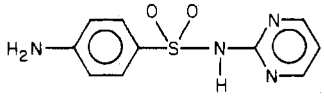
The crystal structure of 2-sulfanilamidopyrimidinesilver(I), $Ag(C_{10}H_9N_4O_2S)$, a burn treatment compound, was determined from single-crystal automated x-ray diffractometer measurements. The crystal data are: $a = 6.173$ (2), $b = 9.600$ (5), $c = 20.30$ (2) Å, $\beta = 96.22$ (8)°, *d*(measured) = 1.982 (3), *d*(calcd) = 1.983, $Z = 4$, $P2_1/c$, 1719 total reflections, 1151 present, $R_1 = 0.053$, $R_2 = 0.031$, from full matrix least squares. The nitrogen atoms of the pyrimidine ring coordinate to two different silver atoms to form polymeric chains extending through the crystal. Each silver atom in this chain is also coordinated to one oxygen atom from the sulfonyl group of the 2-sulfanilamidopyrimidine molecule in the chain. A second identical chain (related by center of symmetry) is joined to the first chain by the coordination of the silver atom from each chain to the imido nitrogen atom of the 2-sulfanilamidopyrimidine molecule in the other chain. In addition, the silver atoms in one chain are only 2.916 (1) Å from the symmetry-related silver atom in the other chain. The double stranded chains are further hydrogen bonded by the amine hydrogen atoms and sulfonyl oxygen atoms to form planar sheets of the double-stranded chains. The coordination about silver is a distorted trigonal bipyramid.

Introduction

The crystal structure of 2-sulfanilamidopyrimidinesilver(I), a burn treatment compound, was undertaken to determine the coordination about silver and to verify the presence or absence of the imido hydrogen atom. [The common name for 2-sulfanilamidopyrimidine is sulfadiazine; for brevity, the complex will be called silver sulfadiazine in the text.] Silver sulfadiazine is too insoluble in alcohol to permit a good NMR spectrum; in dimethyl sulfoxide the spectrum is ambiguous due to decomposition to form a silver mirror and peak broadening from nitrogen quadrupole coupling. Powder diagrams of silver sulfadiazine made by treating sodium sulfadiazine with silver nitrate and by treating sulfadiazine directly with silver nitrate are identical. This observation coupled with the crystal structure described below indicates that it is Ag(I) which is complexed and that the imido hydrogen atom is absent.



2-sulfanilamidopyrimidine ≡ sulfadiazine

Experimental Section

Crystals of silver sulfadiazine were made by mixing two 500-ml solutions of approximately 2×10^{-3} M sulfadiazine and silver nitrate in boiling 95% ethyl alcohol and cooling the solution from 63 °C to room temperature over a 12-day period in a 50-l. water bath. Chemical analysis of the crystals gave the following. Found [theoretical]: Ag, 30.22 (3) [30.20%]; C, 33.3 (3) [33.6%]; N, 15.7 (1) [15.7%]; H, 1.9 (3) [2.5%].

The colorless crystals are monoclinic, space group $P2_1/c$ with $a = 6.173$ (2) Å, $b = 9.600$ (5) Å, $c = 20.30$ (2) Å, $\beta = 96.22$ (8)°, $V = 1195.86$ Å^3; *d*(pycnometrically) = 1.982 (3) g/cm^3, *d*(from cell dim) = 1.983 with $Z = 4$, formula weight for $C_{10}H_9N_4O_2SAg$ = 357.15, $F_{000} = 352$. Linear absorption coefficient = 17.8 cm^{-1}. The cell dimensions were determined from 12 reflections with 2*θ* between 32 and 45° with Mo Kα_1 = 0.70926 Å.

Intensity data were obtained by the 2*θ* scan method on a Picker diffractometer. Background counts were made for 10 s on each end of the scan of 1.5°, scan rate = 1°/min; oriented graphite monochromated Mo K*α* radiation was used. The integrated intensity and standard deviation in the net intensity were calculated as in previous work.[1] Lorentz and polarization corrections were made, but an absorption correction was not made since the absorption correction would range only between the limits of 0.88 to 0.98. The crystal, 0.01 mm along *b**, 0.06 mm along *c**, and 0.59 mm along *a**, was mounted with its rotation axis approximately along *a**.

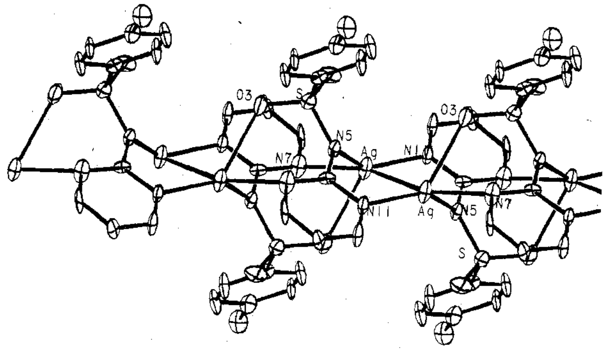


Figure 1. Structure of 2-sulfanilamidopyrimidinesilver(I) showing the interlinked double-stranded chain.

Nonhydrogen-scattering factors and dispersion corrections were taken from ref 2, and the hydrogen scattering factors used were those of Stewart, Davidson, and Simpson.[3] The real portion of the dispersion correction to the scattering factors of silver and sulfur was included in all calculations, and the imaginary part was included in the last two cycles of refinement.

The structure was solved using heavy-atom techniques. Least-squares refinements were initially by block-diagonal methods, but the last cycles were by full-matrix methods. The initial difference map to locate hydrogen atoms (after isotropic refinement $R_1 = 0.09$) showed all hydrogen atoms except one from the pyrimidine ring, one from the phenyl ring, one from the amino group, and one from the imido hydrogen. Including hydrogen atoms in the structure factor calculation did not significantly lower the discrepancy factor at this stage in refinement.[4] Weights used during refinement were the reciprocals of the variances of the observed structure factors; they ranged from 0.01 to 5.4. Absent reflections were given a rather arbitrary weight of 1.0 to force the parameters to correspond to these data, as a rather conservative criterion was used in establishing present reflections.[1] The discrepancy factors, $R_1 = 0.0533$ and $R_2 = 0.0306$, were obtained on the final least-squares cycle which refined on anisotropic temperature factors for all atoms except hydrogen, all coordinates except hydrogen, included all anomalous dispersion corrections, and assumed the imido hydrogen atom was absent. The values of the variables

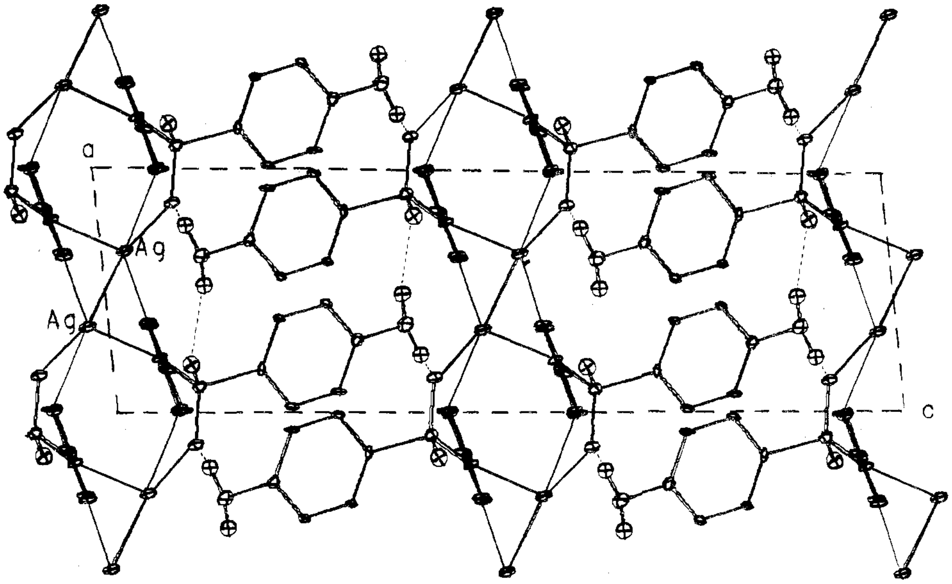


Figure 2. A view of the structure of 2-sulfanilamidopyrimidopyrimidinesilver(I) approximately along the *b* axis. Dotted lines indicate possible hydrogen bonds. Dashed lines indicate the unit cell. The projection axis lies in the plane of the pyrimidine ring; thus, these atoms are superimposed in this projection.

Table I. Final Positional Parameters for Nonhydrogen Atoms[a]

	x	*y*	*z*
Ag1	−3421 (1)	1027.8 (0.8)	279.9 (0.4)
S2	977 (3)	−972 (3)	1072 (1)
O3	−1410 (8)	−945 (7)	949 (2)
O4	1904 (9)	−234 (5)	997 (3)
N5	2174 (9)	51 (7)	605 (3)
C6	1911 (13)	1439 (8)	638 (4)
N7	21 (10)	2033 (7)	793 (3)
C8	−20 (13)	3397 (9)	829 (4)
C9	1652 (12)	4242 (9)	686 (4)
C10	3503 (13)	3559 (9)	517 (4)
N11	3665 (9)	2206 (7)	490 (3)
C12	1716 (13)	−363 (8)	1879 (4)
C13	156 (12)	333 (10)	2213 (4)
C14	800 (11)	913 (11)	2824 (4)
C15	2941 (12)	779 (10)	3120 (4)
C16	4440 (12)	59 (11)	2774 (4)
C17	3817 (12)	−512 (10)	2159 (4)
N18	3604 (10)	1308 (7)	3748 (3)

[a] All fractional values of the unit cell dimensions are multiplied by 10^4. Estimated standard deviations are given in parentheses.

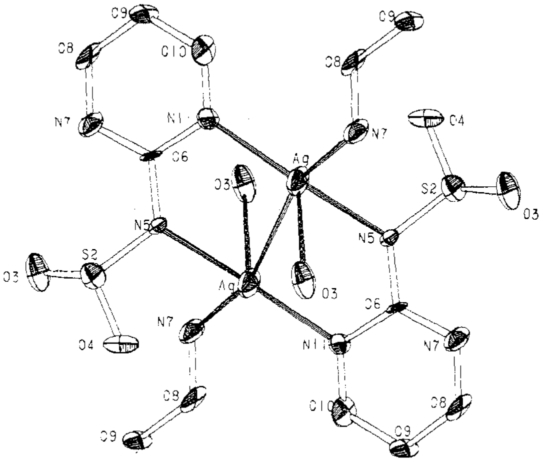


Figure 3. Distorted trigonal-bipyramidal coordination about the silver atom.

changed less than 1% of the estimated standard deviation of that variable in the last cycle. The final atom parameters are given in Table I.[5]

Discussion

The nitrogen atoms of the pyrimidine ring coordinate [2.459 (6) and 2.205 (6) Å] to two different silver atoms to form polymeric chains extending through the crystal in the *a* direction (Figure 1). Each silver atom in this chain is also coordinated to one oxygen atom [2.571 (6) Å] of a sulfonyl group of the sulfadiazine molecule in the chain. A second identical chain (related by the center of symmetry) is joined to the first chain by coordination of the silver atom from each chain to the imido nitrogen atom [2.277 (6) Å] from the sulfadiazine molecule in the opposite chain. In addition, in the fifth coordinate position about Ag, the silver atom in the opposite chain is only 2.916 (1) Å away. Hydrogen bonds between the amine hydrogen atoms and the other sulfonyl oxygen atom link the double-stranded chains together in the *b* and *c* directions (Figure 2).

The configuration around each silver atom is a distorted trigonal bipyramid (Figure 3). The N7–Ag–Ag angle is bent (162.2°) and the O3 position in the O3–N11–N5 equatorial plane is tilted toward the N7 apex. The sum of the equatorial angles is 351°, and the central silver atom is 0.38 Å from the equatorial plane. The three equatorial angles show similar deviations from the ideal 120° [84.1, 129.3, 137.6°] as do the comparable angles in silver sulfimide trihydrate [103, 123, 133°],[6] cyclooctatetraenesilver(I) nitrate [80, 132, 132°],[7] and norbornadienesilver(I) nitrate [85, 130, 130°].[8]

Short Ag–Ag distances have been observed in other structures, 3.032 Å in silver sulfimide trihydrate;[6] 2.94 and 3.29 Å in piperazinesilver(I) iodide,[9] 2.986–3.095 Å in piperidinesilver(I) iodide,[10] and 2.853 and 2.893 in silver trifluoroacetate benzene,[11] and the distance in silver metal is 2.888 Å.[12] Since a short distance does not necessarily mean that a bond is formed, one can examine what the consequences of assuming the presence of a Ag–Ag bond would be. The two chains of silver–diazine linkages are adequately cross-linked by the imido nitrogen atoms, and a Ag–Ag bond is not needed to hold the two chains together. The assumption of the Ag–Ag bond does provide, however, a qualitative explanation of the bond distances of silver from its surrounding ligands.

If a set of four-center molecular orbitals is formed from the p orbitals of N7–Ag–Ag–N7, and if one makes the simplifying assumption that all these p orbitals are identical, then filling

Table II. Bond Distances and Angles[a]

Ag–Ag	2.916(1)	C9–C10	1.397 (11)
Ag–N5	2.277(6)	C10–N11	1.304 (10)
Ag–N7	2.459(6)	N11–C6	1.370 (9)
Ag–N11	2.205(6)	C12–C13	1.405 (10)
Ag–O3	2.571(6)	C13–C14	1.379 (10)
S2–O3	1.467 (5)	C14–C15	1.397 (9)
S2–O4	1.448(6)	C15–C16	1.403 (10)
S2–N5	1.600(6)	C16–C17	1.379 (10)
S2–C12	1.753 (7)	C17–C12	1.366 (9)
N5–C6	1.345(9)	N18–C15	1.393 (9)
C6–N7	1.366(9)	N18–O3	3.057 (9)
N7–C8	1.311(9)	N18–O4	3.055 (9)
C8–C9	1.369(11)		

Group or central Atom	Angle	Degree
Imido nitrogen	S2–N5–Ag	114.0 (3)
	C6–N5–Ag	122.9 (5)
	S2–N5–C6	120.8 (6)
Diazine nitrogen N7	C8–N7–Ag	113.3 (6)
	C6–N7–Ag	117.3 (5)
Diazine nitrogen N11	C10–N11–Ag	125.8 (6)
	C6–N11–Ag	116.6 (5)
Diazine ring	C6–N7–C8	116.9 (7)
	N7–C8–C9	124.1 (8)
	C8–C9–C10	115.6 (8)
	C9–C10–N11	123.0 (8)
	C6–N11–C10	117.6 (7)
	N7–C6–N11	122.8 (7)
	C17–C12–C13	123.3 (7)
Phenyl ring	C12–C13–C14	118.7 (7)
	C13–C14–C15	121.1 (8)
	C14–C15–C16	118.3 (7)
	C15–C16–C17	120.9 (7)
	C16–C17–C12	119.6 (7)
Amino	C14–C15–N18	122.0 (7)
	C16–C15–N18	119.6 (7)
Trigonal-bipyramidal configuration around silver	Ag–Ag–N7	160.2 (2)
	O3–Ag–N5	84.1 (2)
	O3–Ag–N11	129.3 (2)
	N5–Ag–N11	137.6 (2)
	N11–Ag–N7	113.7 (2)
	N7–Ag–N5	99.3 (2)
	O3–Ag–N7	73.7 (2)
	Ag–Ag–O3	88.4 (1)
	Ag–Ag–N5	69.8 (1)
	Ag–Ag–N11	84.1 (2)
Sulfur	O3–S2–O4	113.5 (4)
	N5–S2–C12	105.1 (4)
	O3–S2–C12	107.9 (4)
	O3–S2–N5	114.1 (3)
	O4–S2–N5	106.4 (3)
	O4–S2–C12	109.5 (4)
Oxygen	S2–O3–Ag	121.4 (4)

[a] Estimated standard deviations in the last significant figure are given in parentheses.

the two lowest energy orbitals would lead to a 5/6 order bond between the silver atom and the terminal nitrogen atoms and a 1/3 order bond between the silver atoms. It is observed that the apex silver–nitrogen bond distance [2.459 (6) Å] is significantly longer than the equatorial distances [2.205 (6) and 2.277 (6) Å]. The combination of the electron-deficient character of the apical bond and its p character as compared to the more sp^2-like character of the equatorial bonds accounts for the observed distances. Similarly, the bond distance between the silver atoms is reasonable for 1/3 bond order.[13]

The imido nitrogen atom is connected to the sulfur atom, the pyrimidine ring, and the silver atom with the sum of the three bond angles [114.0, 122.9, 120.8°] being 357.7°. With essentially trigonal planar coordination, it seems unlikely that a hydrogen atom is attached, since the angles should then be more nearly tetrahedral. The planarity of the coordination about the nitrogen atom plus the preparation of the complex from sodium sulfadiazine and the absence of the H atom from the electron density difference maps all support the absence of a H atom on the imido nitrogen atom.

Note Added in Proof. The authors have just become aware of an independent crystal structure determination of silver sulfadiazine.[14]

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Supplementary Material Available: A table of temperature fctors (Table III) and a listing of structure factors (Table IV) (21 pages). Ordering information is given on any current masthead page.

References and Notes

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(5) The positional parameters are given fully in the text. The temperature factor parameters are given as Table III in the supplementary material. The observed and calculated structure factors are given as Table IV in the supplementary material.
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(13) Although the short Ag–Ag distance in the silver trifluoroacetate benzene complex was attributed to the small coordinate "bite" of the O–C–O grouping, that structure also presents opportunities for the four-center bonds. The oxygen atoms in the bidentate coordination group are planar three coordinate [bond angles of 99, 122, and 139°; 101, 124, and 134°]. The nonequality of the two C–O–Ag angles can be explained by attributing the smaller of the two C–O–Ag angles to Ag1–Ag1′ and Ag2–Ag2′ interactions. The Ag–O bond distances which would be involved in the four-center bonds are 2.38 and 2.43 Å compared to the distances of 2.22, 2.23, 2.28, and 2.41 Å for the Ag–O bond distances not involved in the four-center bonds. It also should be noted that the shorter Ag–O bond distances in this structure are comparable to the shorter Ag–N distances in the silver sulfadiazine complex.
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