

Les paramètres A et R_0 ont été déduits en première approximation des tables de rayons ioniques de Shannon & Prewitt (1969). Les valeurs de S_j , calculées pour les polyèdres de coordination des ions, sont résumées dans le Tableau 4. Nous avons également fait figurer dans ce tableau la valence qui s'en déduit pour chaque ion $V = \sum S_j$.

L'examen de ce tableau montre que la somme des valences totales des cations de la structure est de 118,4 au lieu de 120 pour les soixante atomes d'oxygène, ce qui nous paraît une bonne approximation.

Il montre également que les atomes d'oxygène mis en commun pour former les octaèdres vides de la couche A sont fortement liés aux rhodiums voisins. Le polyèdre des atomes de rhodium Rh(4) en site 12(*i*) a une arête commune avec l'octaèdre vide et deux forces de liaison de 0,73.

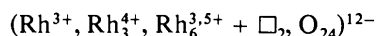
Pour le rhodium Rh(2) en site 8(*h*), dont le polyèdre de coordination a trois arêtes communes, les trois forces de liaison sont de 0,57.

Le polyèdre de l'atome de rhodium Rh(3) placé en site 6(*f*) a quatre atomes d'oxygène communs avec l'octaèdre vide et quatre forces de liaison de 0,68.

Ces résultats impliquent pour les oxygènes du polyèdre vide une valence moyenne calculée de 1,98.

Le Tableau 4 met également en évidence une valence moyenne de 3,41 pour le rhodium en bon accord avec l'équilibre électrostatique de la formule $(Rh_{28}^{3,43+}O_{60})^{24-}Pb_{12}^{2+}$. Cependant, compte-tenu de la somme des erreurs calculées $\Delta\Sigma = \sum \Delta S_j$ pour chaque atome, il apparaît clairement que les atomes de rhodium Rh(1) et Rh(2) placés en site 2(*b*) et 8(*h*) sont des atomes trivalents et que le site 6(*f*) est occupé par des atomes de rhodium Rh(3) tétravalents. Par contre, les atomes de rhodium Rh(4) placés en site 12(*i*) ont une valence proche de 3,5 impliquant pour ce site une distribution statistique de 1 Rh^{3+} pour 1 Rh^{4+} .

L'étude des forces de liaison permet donc de formuler les couches A



et de manière formelle, l'ensemble de la structure:



Dans cette structure, le rhodium se trouve à une valence moyenne inhabituelle de 3,43. Ce fait nous incite à prendre comme hypothèse de travail l'existence de phases analogues où le rhodium serait à la valeur habituelle 3+ pouvant se formuler: $(Rh_3^{3+}O_{15})^{9-}Pb_{1,5}^{2+}M_{1,5}^{4+}$.

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Structure of Tetrasilver(I) Sulfamide

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Abstract

$Ag_4SO_2N_2$ forms deep-red crystals, space group $Pna2_1$, with $Z = 4$, $a = 10.42$ (1), $b = 5.78$ (1), $c = 8.95$ (1) Å.

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The structure was solved by a combination of direct methods and Fourier techniques. Six models differing with respect to the assignment of the N and O atoms of the sulfamide group were refined and the results

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analyzed in terms of the R -factor ratio. The structure consists of a network of sulfamide groups linked by covalently bonded Ag atoms. With the exception of one Ag—O bond, all Ag atoms are coordinated to the N atoms of the sulfamide group. One of the N atoms shows an unusual five-coordination.

Introduction

Ag^I sulfamides show an interesting dependence of color on Ag content: disilver sulfamide (Nachbaur, Popitsch & Burkert, 1974; Greschonig, Nachbaur & Krischner, 1977) is colorless; trisilver sulfamide (Nachbaur & Popitsch, 1973) is yellow; and tetrasilver sulfamide (Nachbaur & Popitsch, 1973) is deep red. Fig. 1 shows a plot of the average of the two SO stretching frequencies *versus* the frequency of the long-wavelength UV/VIS absorption band (Popitsch, 1980). On the basis of the concept of Pitzer & Hildebrand (1941), Donohue & Helmholz (1944) interpreted the color of Ag^I compounds (phosphate, arsenate, carbonate) in terms of the distance between Ag and O, which was taken to be a measure of the covalent character of the Ag—O bond. Although there are now several examples which appear to contradict this simple correlation between depth of color and Ag—O distance (Barclay & Hoskins, 1963; Acland & Freeman, 1971; Sabrowsky & Hoppe, 1968) the concept as such still seems to be accepted (Palmer, 1965; Trotman-Dickenson, 1973).

The crystal structure of colorless disilver(I) sulfamide was determined by Greschonig, Nachbaur & Krischner (1977). In this crystal each Ag atom is bonded to two N atoms (Ag...N 2.12–2.2 Å) of different SO₂N₂ tetrahedra, leading to the formation of double chains. The lower electronegativity of N compared to O makes the exclusive coordination of Ag^I to the N atoms plausible. We have determined the crystal structure of tetrasilver(I) sulfamide (hereafter Ag₄SA) to obtain a structural explanation of the color

of this compound, possibly in terms of the coordination between Ag and sulfamide.

Experimental

Ag₄SA was synthesized as described by Nachbaur & Popitsch (1973). The microcrystals obtained were subsequently suspended in alcohol and treated with gaseous ammonia, which converted the Ag₄SA into the yellow Ag₄SA·2NH₃. Treatment with boiling aqueous AgClO₄ (20%) yielded deep-red, transparent Ag₄SA single crystals. These are insensitive to atmospheric influences, but decompose vigorously when mechanical stress or an electric current is applied. They are insoluble in all common solvents. Magnetic measurements indicate diamagnetism, which depends on field strength and temperature (Haselmair, 1979).

Cell dimensions were determined by least squares from the setting angles of seven reflections on a Stoe four-circle diffractometer. A small wedge-shaped crystal bounded by the faces (010) ($d = 0.02$ mm), ($\bar{1}\bar{1}0$) ($d = 0.026$ mm), ($1\bar{1}0$) ($d = 0.026$ mm), (012) ($d = 0.045$ mm), (012) ($d = 0.045$ mm) was chosen, and the distances d of the bounding planes from an arbitrary reference point were determined under a microscope.

Intensity measurements were carried out in the ω -scan mode, with graphite-monochromated Mo K radiation ($\lambda = 0.71069$ Å). The intensity was integrated over an ω range of 1.6°; a measuring algorithm was employed which attempted to record the intensity of every significant reflection with a statistical significance at least 25σ above background. All reflections in one octant of reciprocal space with $2\theta \leq 60^\circ$ ($\sin \theta/\lambda \leq 0.704$ Å⁻¹) were recorded, yielding 953 reflections (including 118 systematically extinct reflections).

Data reduction involved Lp correction and a numerical absorption correction [program *ABSORB* of the XRAY system (Stewart, 1976)] ($\bar{\mu} = 14.49$ mm⁻¹). Of the 835 non-extinct reflections, 772 had $|F_o| > 3\sigma(|F_o|)$. The choice between the two possible space groups compatible with the observed systematic absences ($Ok\bar{l}: k + l = 2n + 1$; $h0l: h = 2n + 1$; $Pna2_1$ or $Pnma$) was made on the basis of the intensity distribution, which clearly indicated a noncentrosymmetric structure. The positions of the four Ag atoms were determined with *MULTAN* (Germain, Main & Woolfson, 1970). The remaining atoms were obtained from a Fourier synthesis. Since, at that point, it was not possible to distinguish N from O, the subsequent refinement was carried out with four identical ligands, the scattering factors of the light atoms being taken as the average of the N and O factors. After full-matrix least-squares refinement with isotropic temperature factors for all atoms and then

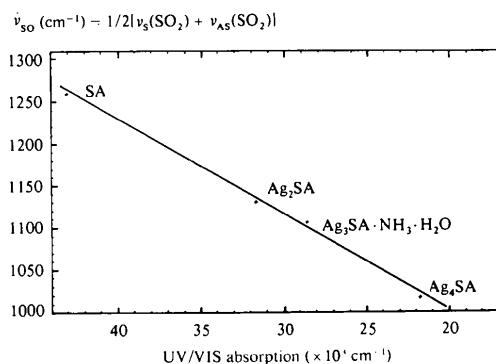


Fig. 1. IR frequencies *versus* long-wavelength UV/VIS absorption frequencies for several Ag^I sulfamides.

anisotropic for Ag and S ($1/\sigma$ weights in the terminal refinement cycles), convergence was reached at $R = 0.033$.

The four ligands differ with respect to their coordination to Ag. The highest coordinated ligand [L(1)] has four adjacent Ag atoms, L(2) has three, L(3) has one and L(4) has no Ag atom within 2.2 Å. This fact and the bonding distances between S and its ligands [S–L(1) 1.63, S–L(2) 1.57, S–L(3) 1.49, S–L(4) 1.48 Å] suggested the assignment L(1) = L(2) = N, L(3) = L(4) = O, a choice which agrees with what is expected on the basis of the electronegativity of N and O and with the atom assignment in the X-ray structure of Ag₂SA. However, the coordination of N and O with Ag^I was one of the questions which motivated this analysis, and we therefore attempted to distinguish N and O on the basis of our crystallographic evidence alone.

Since the scattering factors for N and O decrease more rapidly with increasing scattering angle than does that of Ag⁺, we excluded reflections with $\sin \theta/\lambda \geq 0.52 \text{ \AA}^{-1}$ for all refinements described in this paragraph. This left a data set with 312 observed reflections. There are six possible orientations of the sulfamide group in the crystal, corresponding to six different atom assignments. Each of these crystal structures plus the model with four identical ligands (each atom consisting of 50% N and 50% O, labeled X below) was refined with respect to the restricted data set ($1/\sigma$ weights); isotropic temperature factors were refined for the sulfamide group, anisotropic for Ag. The resulting R factors are listed below.

Atoms bound to S				$R_1 =$	$R_2 =$
L(1)	L(2)	L(3)	L(4)	$\frac{\sum F_{ot} - F_{ct} }{\sum F_{ot} }$	$\frac{\sum w_i (F_{ot} - F_{ct})^2}{\sum w_i F_{ot} ^2}$
X	X	X	X	0.02411	0.000811
N	N	O	O	0.02422	0.000800
O	O	N	N	0.02458	0.000859
N	O	N	O	0.02417	0.000806
O	N	O	N	0.02459	0.000842
O	N	N	O	0.02471	0.000842
N	O	O	N	0.02442	0.000824

Rothstein, Richardson & Bell (1978) have pointed out that Hamilton's (1965) R-factor test can be applied to atom-assignment problems if the dimension of the hypothesis is taken to be unity. This test indicates that the NNOO assignment is preferred over any other possibility at a 0.05 significance level or better. To obtain a clearer discrimination between the two best structures (NNOO and NONO), these two structures were subsequently refined against the full data set, with anisotropic factors for S and Ag. The result (NNOO: $R_2 = 0.00152$; NONO: $R_2 = 0.00156$) confirms the preference for the NNOO assignment, now at a considerably better significance level ($\alpha < 0.005$).

Although the result is unambiguous in a statistical sense, there are several qualifications which should be noted: (1) the R-factor test is not a robust test, being sensitive to non-statistical errors in one or a few reflections; (2) attempts to refine the N and O atoms anisotropically invariably led to negative temperature factors for at least one ligand; (3) the distribution of temperature factors in the hypothetical XXXX structure would suggest the OONN assignment rather than

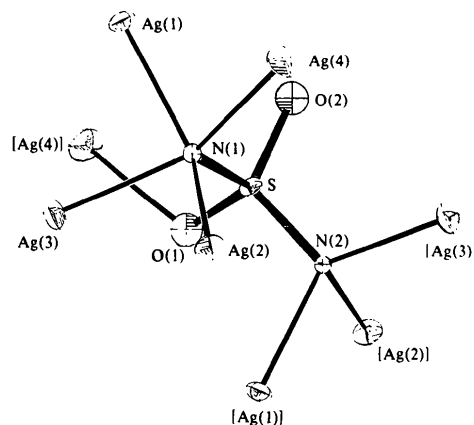


Fig. 2. Projection of one sulfamide molecule with its eight nearest Ag^I neighbors onto the XY plane. Atoms in square brackets belong to different asymmetric units.

Table 1. Fractional atomic coordinates and vibrational tensor components ($\times 10^4$, U values in Å²) for tetrasilver(I) sulfamide

For atoms refined isotropically the temperature factor is of the form $T = \exp[-(8\pi^2 U_{iso} \sin^2 \theta/\lambda^2)]$; for atoms refined anisotropically it is of the form $T = \exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12} + \dots)]$. E.s.d.'s (in parentheses) are in units of the last significant figure.

	x	y	z	U_{iso} or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	6829 (27)	2485 (51)	5837 (32)	72 (51)					
N(2)	5352 (27)	-855 (50)	4755 (34)	68 (51)					
O(1)	5807 (31)	2615 (61)	3282 (39)	225 (66)					
O(2)	7581 (31)	-44 (61)	3738 (40)	221 (65)					
S	6402 (8)	990 (16)	4370 (10)	71 (33)	110 (38)	70 (36)	-25 (29)	5 (32)	-30 (33)
Ag(1)	8594 (2)	4276 (5)	5411 (0)	91 (10)	160 (11)	177 (12)	-35 (9)	-3 (11)	41 (12)
Ag(2)	5565 (3)	2022 (5)	7771 (5)	146 (11)	204 (13)	117 (11)	-26 (11)	34 (11)	31 (11)
Ag(3)	5996 (3)	5960 (5)	5682 (5)	219 (13)	123 (12)	352 (19)	56 (11)	28 (14)	57 (14)
Ag(4)	8069 (3)	180 (6)	7163 (6)	214 (14)	278 (16)	297 (17)	51 (13)	-34 (14)	173 (15)

NNOO $\{B[L(1)] = 0.93, B[L(2)] = 0.85, B[L(3)] = 1.43, B[L(4)] = 1.37 \text{ \AA}^2\}$; (4) the physically unreasonable *XXXX* structure yields a residual ($R_2 = 0.00148$) which is even better than that of the NNOO structure ($R_2 = 0.00152$), when refined against the full data set.

It appears that the observed temperature factors have taken up errors which were insufficiently accounted for by the absorption correction. The large absorption coefficient makes an accurate absorption correction difficult. Nevertheless, the crystallographic evidence favors the (chemically most reasonable) assignment NNOO. The coordinates and temperature factors listed in Table 1 correspond to this structure, refined against the full data set with $1/\sigma(F_o)$ weights ($R = 0.033$).*

Discussion

Fig. 2 shows a projection of one sulfamide molecule with its eight nearest Ag neighbors, projected on to the *XY* plane. The bonding geometry is indicated in Fig. 3.

N(1) is located in the interior of a square-pyramidal coordination shell, consisting of a S atom and four Ag atoms. Likewise, N(2) is located inside a distorted trigonal pyramid. Each Ag atom is bonded to two N atoms [or one N and one O: Ag(4)] in a more or less linear arrangement. This gives rise to a complicated three-dimensional network of sulfamide molecules connected through Ag atoms. No pair of sulfamide

molecules shares more than one common Ag atom. O(2) is not bonded to any Ag atom: its closest Ag neighbor is 2.71 Å away; O(1) is bonded to only one Ag atom, its next-nearest Ag neighbor is at 2.90 Å. Both distances are beyond the 2.1–2.2 Å observed for the (covalent) Ag–N and Ag–O distances.

There are several short Ag–Ag contacts. Ag atoms bonded to the same N come as close as 2.87 Å [coordination around N(1): Ag(1)···Ag(3) 2.89, Ag(1)···Ag(4) 2.89, Ag(2)···Ag(4) 2.87 Å; coordination around N(2): Ag(1)···Ag(2) 2.98 Å]; the closest Ag–Ag distance between atoms not sharing a common N atom is 3.04 Å.

The bonding geometry around the Ag atoms is in agreement with the geometry of covalent Ag–N and Ag–O bonds in related structures. The five-coordination around N(1), however, is not the coordination expected for an sp^3 -hybridized N atom. Coordination numbers exceeding four are only observed in nitrides (Wells, 1975; Hahn & Gilbert, 1949), which makes Ag_4SA an intermediate between purely covalent Ag^I compounds (like Ag_2SA) and the class of interstitial compounds, whose structure appears to be dominated by metal–metal interactions. Thus, the distances between the Ag atoms around N(1) agree with the Ag–Ag distance found in metallic silver (2.88 Å).

A comparison of the Ag_4SA crystal structure with that of Ag_2SA reveals that no explanation for the deep color of the former compound can be given in terms of the concept of Pitzer & Hildebrand (1941) alone. It is certainly true that all colored Ag^I compounds exhibit covalent bonding between Ag and N (or O), but there are examples of colorless compounds which also have short Ag–N or Ag–O bonds (e.g. Ag_2SA). We believe that the appearance of color in Ag^I compounds is the result of a cooperative interaction between several Ag atoms. It is a remarkable fact that all colored Ag^I compounds show a very high Ag content.

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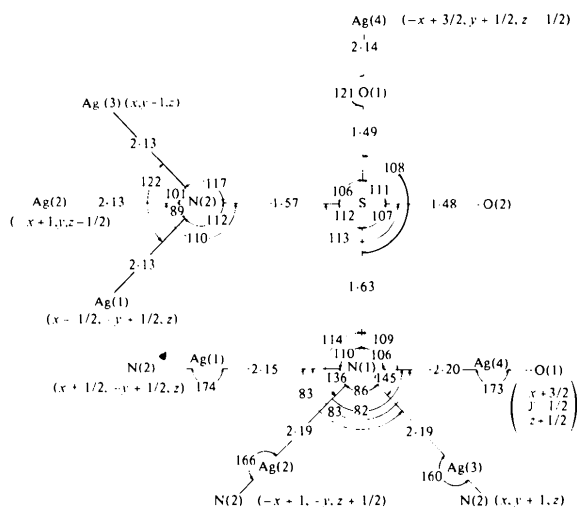


Fig. 3. Bonding geometry in the tetrasilver(I) sulfamide crystal structure.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35095 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Etude Structurale des Polytypes à Deux Anions $LSeF$ ($L = Y, Ho, Er \dots$). V. Structure du Polytype Orthorhombique à Quatorze Couches du Fluoroséléniure d'Yttrium 'YSeF' 14O

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Abstract

The structure of a fourteen-layer polytype 14O 'YSeF' [$a = 9.919$ (6), $b = 43.99$ (2), $c = 4.095$ (3) Å, $Z = 28$, orthorhombic, space group $Pnam$, $D_m = 4.81$, $D_x = 4.86$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 34.15$ mm⁻¹] was refined by the least-squares method to a final $R = 0.06$. The stacking sequence observed in this polytype is ...SSSTSTSTTTSTST... where S and T layers are related to each other by a glide plane a . It has been shown that the so-called anion X site is partially occupied by O and F atoms, while in $8M$ and $10M$ polytypes this site is occupied by half a statistically disordered O atom.

Introduction

L'étude structurale par diffraction de rayons X et par microscopie électronique à haute résolution des polytypes du fluoroséléniure d'yttrium ou de lanthanides lourds $LSeF$ ($L = Y, Ho, Er \dots$) a montré qu'ils sont constitués de couches dénommées S et T , de composition $LSeF$ et déduites l'une de l'autre par un pseudo-plan de glissement a (Nguyen-Huy-Dung, Dagron & Laruelle, 1975a,b; Van Dyck, Van Landuyt,

Amelinckx, Nguyen-Huy-Dung & Dagron, 1976a,b). Cette alternance de couches S et T dans une matrice régulière $(ST)_n$ est cependant interrompue par une succession de trois couches de même orientation SSS ou TTT dont la périodicité et le nombre déterminent l'ordre et la symétrie de ces polytypes. Ainsi, lorsqu'une triade SSS est exactement compensée par une triade TTT , la structure est orthorhombique ($Pnam$). Sinon, elle devient monoclinique ($P2_1/m$). Un mécanisme de cisaillement périodique permet d'expliquer dans une matrice régulière ...STST... la transformation en triade ...SSST... De plus, lors de l'affinement des structures des polytypes $10M$ et $8M$, le site X situé au centre de la triade ...SSS... qui devrait être normalement occupé par un atome de fluor, ne paraît contenir que quatre à cinq électrons. La substitution d'un demi-atome d'oxygène à un atome de fluor permet d'équilibrer les charges électriques et de rendre compte du caractère diélectrique de ces cristaux qui sont transparents et de couleur jaune pâle (Nguyen-Huy-Dung & Laruelle, 1977a,b). Ce défaut chimique localisé n'a pas encore été mis en évidence dans les polytypes orthorhombiques d'ordre élevé. C'est la raison pour laquelle nous avons entrepris l'étude structurale du polytype 'YSeF' 14O.