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Silver Hydrogen Sulfate, $Ag(O_3SOH)$: Preparation, and the OD Character of the Crystal Structure

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Crystalline $Ag(O_3SOH)$ was produced by reacting Ag_2O or silver sulfate with sulfuric acid. The crystals, which are stable only in an extremely dry atmosphere, show a X-ray diffraction pattern with apparent *mmm* symmetry, with extinction rules inconsistent with any space group and suggestive of the order−disorder (OD) character of the structure. In fact, the specimens studied are monoclinic polytypes, space group $P12_1/c1$, $a = 15.140(3)$ Å, $b = 8.199(1)$ Å, $c = 10.721(1)$ Å, $\beta = 90.00(1)°$, $V = 1330.8(3)$ Å^3, $Z = 16$, of a whole OD family. The OD approach allowed a successful structure solution; the refinement [$R = 4.25\%$, $R_w = 9.37\%$, 1449 observed data $F_0 > 4\sigma(F_0)$] showed four different silver ions having a highly distorted octahedral coordination. The mean Ag−O distance is 2.543 Å and one of the silver cations has a seventh oxygen atom at a distance of 2.84(1) Å. Silver hydrogen sulfate in sulfuric acid solution absorbs carbon monoxide reversibly.

Introduction

The first attempts to crystallize Ag_2SO_4 from H_2SO_4 in order to obtain the hydrogen sulfate derivative date back to last century.[1] In this century, silver sulfate was observed to dissolve in concentrated sulfuric acid giving rise on cooling to solids of different compositions, depending on the silver concentration.[2] A solid of composition $Ag_2SO_4 \cdot 2\ H_2SO_4$ was observed to freeze at temperatures below 39 °C from solutions containing up to 12.4 mol % of Ag_2SO_4. Above this temperature, from more concentrated solutions, solids of composition $xAg_2SO_4 \cdot yH_2SO_4$ were obtained, formally approximating the hydrogen sulfate derivative. Two different salts of composition $Ag_2SO_4 \cdot H_2SO_4$ were prepared, which were identified as the α phase (prismatic crystals, stable at lower temperature) and the β phase (needlelike crystals, stable at higher temperatures), the transition temperature being 66 °C. The high sensitivity of these products to moisture produced a spreading of results even in more recent times. Nazarova and Tsukervanik [3] obtained a solid formulated as $Ag(O_3SOH)$ by melting equimolar amounts of Ag_2SO_4 and H_2SO_4, while other authors[4] explicitly stated that silver hydrogen sulfate cannot be prepared under these conditions. These difficulties convinced later authors to adopt different methods of preparation, such as the reaction of AgO_2CCF_3 with H_2SO_4 in trifluoroacetic acid as solvent[4,5] or the reaction between Ag_2SO_4 and H_2SO_4 in acetonitrile as solvent:[4,6] in the latter case, the acetonitrile-solvated $Ag(O_3SOH)$ was obtained, which was reported[4] to revert to Ag_2SO_4 and H_2SO_4 upon attempts to desolvate the product in vacuo. In view of our current interest[7] in carbonyl derivatives of late transition or post-transition elements, we planned further experiments aimed at verifying the possibility for silver(I) to coordinate carbon monoxide under strictly anhydrous conditions[7] and we therefore decided to reinvestigate the pending problem of silver hydrogen sulfate as a possible appropriate substrate for the carbonylation reaction, either in the solid state or in solution. Further interest in this compound arises from the observation that hydrogen sulfates of d^{10} cations of large size (e.g., cesium) have been found to be proton conductors in the solid state.[8] Moreover, hydrogen sulfate derivatives of transition metal cations are, crystallographically speaking, practi-

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cally unknown substances.[9] Therefore, a study of the solid-state and solution properties of silver hydrogen sulfate, as a member of a largely unexplored class of compounds, appeared to be in order.

It is the purpose of this paper to show that Ag_2O and concentrated sulfuric acid give pure $Ag(O_3SOH)$, which can also be obtained from silver sulfate and sulfuric acid. We report the crystal structure of the title compound, and we show that the X-ray diffraction pattern of the solid shows unusual features indicating the OD character of the structure. We also definitely establish that silver hydrogen sulfate undergoes reversible carbonylation in sulfuric acid solution.

Experimental Section

All the operations were carried out under a protected atmosphere free from moisture with conventional Schlenk tubes. Commercial Ag_2O (Chimet S.p.A.) and H_2SO_4 (96%, Rudi Pont) were used. Manipulation of $Ag(O_3SOH)$ was performed under accurately predried dinitrogen. Silver analyses were carried out by the Volhard method. Hydrogen sulfate analyses were carried out by conventional acid−base titration in water after precipitation of silver ions with an eccess of NaCl.

Preparation of $Ag(O_3SOH)$. (A) From Silver(I) Oxide. Ag_2O (10.0 g, 86.3 mmol of Ag) was added stepwise to concentrated H_2SO_4 (40 cm^3) at room temperature. A rapid reaction was observed with formation of a slightly gray suspension, which was filtered. The solid was washed with two portions of $(MeO)_2SO_2$ (2 × 20 cm^3) and dried in vacuo (3.29 g). The dimethyl sulfate washings, added to the first filtrate, precipitated additional product as colorless needles, which were filtered, washed with $(MeO)_2SO_2$, and dried in vacuo (3.75 g, total yield 40%). Anal. Found: Ag, 51.9; H, 0.4%. Calcd for $HAgO_4S$: Ag, 52.6; H, 0.5%. The final suspension was warmed till complete dissolution of the precipitate and the resulting solution was then cooled slowly to room temperature and gave colorless crystals used for the subsequent X-ray diffractometric study. The solubility of $Ag(O_3SOH)$ in an approximately 1:1 mixture of sulfuric acid and dimethyl sulfate or in concentrated sulfuric acid is about 164 or 334 $g \cdot L^{-1}$, respectively.

(B) From Silver(I) Sulfate. Ag_2SO_4 (11.5 g, 36.9 mmol) was treated under dinitrogen with concentrated H_2SO_4 (45 cm^3). The suspension was warmed until a solution was obtained. The solution was cooled to room temperature and then $(MeO)_2SO_2$ (25 cm^3) was added. Colorless crystals slowly precipitated out. After 10 h the suspension was filtered and the solid was washed three times with $(MeO)_2SO_2$ (3 × 5 cm^3) and dried *in vacuo* (10^{-2} mmHg) at $T \sim 60$ °C (3.52 g, yield 23.3%). A second crop of the salt was obtained from the filtrate (3.84 g, total yield 48.7%). Anal. Found: Ag, 52.9; H, 0.5%. Calcd for $HAgO_4S$: Ag, 52.6; H, 0.5%.

Interaction of $Ag(O_3SOH)$ with CO. Solid $Ag(O_3SOH)$ (2.70 g, 13.17 mmol) was added under a CO atmosphere ($p_{CO} = 1$ atm, $T = 28$ °C), using a gas-volumetric apparatus, to concentrated H_2SO_4 (25 cm^3) presaturated with CO. The solution absorbed 39 cm^3 of CO corresponding to a CO/Ag molar ratio of 0.12. Release of CO under reduced pressure was followed by a new uptake of CO at $p_{CO} = 1$ atm, corresponding to the same CO/Ag molar ratio. No absorption of carbon monoxide was observed on the solid product under similar conditions.

Crystal Structure Determination. The crystals obtained by rapidly adding dimethyl sulfate to the sulfuric acid solution at room temperature are needlelike and possibly the same as those observed by Schultz in 1868[1] and by Kendall and Davidson in 1921.[2]

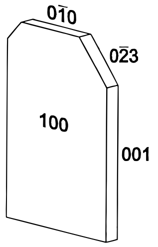

Figure 1. Habit of the $Ag(O_3SOH)$ crystal.

Table 1. Crystal Data and Structure Refinement of $Ag(O_3SOH)$

empirical formula	$HAgO_4S$
formula weight	204.94
temperature (K)	293(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P21/c$ (*n*.14)
unit cell dimensions	
a (Å)	15.140(3)
b (Å)	8.199(1)
c (Å)	10.721(1)
β (deg)	$\beta = 90.00(1)$
volume (Å^3)	1330.8(3)
Z	16
density (calculated) (g/cm^3)	4.091
absorption coefficient (mm^{-1})	6.519
$F(000)$	1536
crystal size (mm)	0.37 × 0.28 × 0.04
θ range for data collection (deg)	1.90−30.00
index ranges	$-1 \le h \le 21, -1 \le k \le 11,$ $-1 \le l \le 15$
reflections collected	2601
independent reflections	2142 [$R_{int} = 3.46\%$]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2140/0/223
goodness of fit[a] on F^2	1.096
final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0425$, $wR_2 = 0.0973$
R indices[a] (all data)	$R_1 = 0.0765$, $wR_2 = 0.1183$
extinction coefficient	0.0077(4)
largest diff peak and hole (e Å^{-3})	0.787 and −0.898

[a] Goodness of fit = $[\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where N, P are the numbers of observations and parameters, respectively, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0544Q)^2 + 1.62Q]$, where $Q = [\mathrm{MAX}(F_o^2,0) + 2F_c^2]/3$.

We have studied the crystal structures of both specimens, finding them to be identical. The needlelike crystals are elongated in the direction normal to (0 $\bar{3}$ 2) and do not show well-defined faces. The tabular crystals, obtained by a temperature gradient (ca. 120−20 °C) from $H_2SO_4/(MeO)_2SO_2$, are well shaped and grow frequently in dimensions of several millimeters. They are elongated in the *b* direction and have their shorter dimension in the *a* direction, as shown in Figure 1. One of the tabular colorless crystals of $Ag(O_3SOH)$, obtained according to the procedure in subsection A, was sealed in a Lindemann capillary under an atmosphere of predried (P_4O_{10}) dinitrogen and its X-ray diffraction was first studied with Weissenberg photographs. It showed orthorhombic symmetry with well-shaped spots. Accurate unit cell dimensions were measured with a four-circle Siemens P4 automatic diffractometer, equipped with a graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å), by centering 20 strong reflections with diffraction angle 2θ between 24.4 and 25°. The intensity data collection was carried out under the experimental conditions summarized in Table 1. During the data collection, three standard reflections were checked every 97 measurements to verify the absence of decay. The data were corrected for Lorentz and polarization effects and for absorption by using a

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Table 2. Atomic Coordinates ($\times 10^4$) for Ag and S Atoms and ($\times 10^3$) for O Atoms and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $Ag(O_3SOH)$[a]

	x	y	z	U_{eq}
Ag(1)	1261(1)	61(2)	1882(1)	26(1)
Ag(2)	1123(1)	5058(2)	1545(1)	28(1)
Ag(3)	3843(1)	22(2)	9232(1)	36(1)
Ag(4)	3758(1)	5034(2)	9202(2)	44(1)
S(1)	3130(4)	7440(5)	1715(5)	23(1)
O(11)	396(1)	746(1)	80(1)	33(4)
O(12)	346(1)	745(1)	297(2)	33(4)
O(13)	264(1)	888(2)	144(1)	43(4)
O(14)	265(1)	604(2)	146(1)	40(3)
S(2)	1861(4)	2325(5)	9254(4)	18(1)
O(21)	106(1)	235(1)	835(1)	27(3)
O(22)	238(1)	366(2)	878(1)	39(3)
O(23)	150(1)	247(1)	1051(1)	24(4)
O(24)	229(1)	72(1)	903(1)	28(3)
S(3)	686(4)	7592(4)	9179(5)	18(1)
O(31)	169(1)	764(2)	899(2)	31(4)
O(32)	53(1)	769(2)	1053(1)	24(3)
O(33)	44(1)	601(2)	869(1)	30(3)
O(34)	32(1)	895(2)	849(1)	32(3)
S(4)	4332(4)	2521(4)	1713(5)	23(1)
O(41)	329(1)	253(1)	154(2)	28(4)
O(42)	467(1)	399(2)	113(1)	37(4)
O(43)	463(1)	99(2)	116(1)	34(3)
O(44)	446(1)	250(1)	309(1)	34(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Gaussian method[10] based on crystal shape and dimensions. The equivalent reflections were then merged; the internal R value ($\Sigma|F_o^2 - F_o^2(\text{mean})/\Sigma(F_o^2)$) was 3.46%.

The structure has been solved through the procedures of the OD theory,[11] as explained in the following. The silver atoms were located by the Patterson method of the SHELXTL package.[10] The Fourier map, calculated by using the four silver atoms as phasing agents, showed the positions of all the heavy atoms. The hydrogen atoms were introduced in calculated positions, bonded to the oxygen atoms having the greatest distances from sulfur, and refined with constraints. The final full-matrix least-squares refinement cycle gave the reliability factors shown in Table 1. Final atomic coordinates are listed in Table 2.

Distances and angles were calculated by using the PARST97[12] program.

OD Character and Derivation of the OD Groupoid Family. Following the basic statements of the theory,[11] OD structures contain neighboring layers which can be arranged in two or more geometrically equivalent ways. The existence of two or more different ways of connecting neighboring layers makes it possible to obtain a family of structures with variable degrees of order. The symmetry features common to all members of the same family are dealt with by the OD theory, which focuses on the space transformations converting any layer into itself or into the adjacent one. Such space transformations are the so-called λ- and σ-PO's (partial operations), respectively; as suggested by their name, they are not necessarily valid for the whole structure.

The common symmetry properties of a whole family are fully described by the so-called "OD groupoid family" symbolized as

$$\begin{array}{llll} P & m & m & (2) \\ & \{n_{s,2} & n_{2,r} & (2_2)\} \end{array}$$

The first line presents the λ-operations (symmetry operations of the single layer, corresponding to one of the 80 layer groups), while the second line presents the σ-operations. The parentheses on each line indicate that only the basic vectors $\mathbf{a}$ and $\mathbf{b}$ are translation vectors corresponding to the periodicities of the single layer, whereas $\mathbf{c_0}$ is not a translation vector. In the example, the single layer has primitive lattice, mirror planes normal to $\mathbf{a}$ and to $\mathbf{b}$ and a 2-fold axis parallel to $\mathbf{c_0}$. The σ-operations (second line) are as follows: n glide normal to $\mathbf{a}$, with translational component $s\mathbf{b}/2 + \mathbf{c_0}$; n glide normal to $\mathbf{b}$, with translational component $\mathbf{c_0} + r\mathbf{a}/2$; a 2-fold screw with translational component $\mathbf{c_0}$. It is appropriate to recall that the most general glide operation is denoted as $n_{r,s}$: the order of the indices in the symbol is chosen in such way that the direction to which n and the two indices refer follow each other in a cyclic way. The indices r and s are only of interest *modulo* 2, so that r may be replaced by $r + 2$ or $r - 2$ and similarly s by $s + 2$ and $s - 2$.

The various disordered and ordered structures display diffraction patterns with common reflections (family reflections present the same position and intensities in all OD structures of the same family) and can be distinguished on the basis of the position and intensities of the other reflections. The family reflections are always sharp, whereas the other reflections may be more or less diffuse, sometimes appearing as continuous streaks. The family reflections correspond to a fictitious structure, periodic in three dimensions, closely related to the structures of the family and called "superposition structure". Two basic vectors of the "superposition structure" are chosen collinear with the translation vectors of the single layer. If, as in the example presented here, the translation vectors are $\mathbf{a}$ and $\mathbf{b}$, the vectors $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ of the "superposition structure" are such that $\mathbf{a} = q\mathbf{A}$ and $\mathbf{b} = t\mathbf{B}$, (q and t are integer numbers) and $\mathbf{C} = p\mathbf{c_0}$.

In the case of silver hydrogen sulfate $Ag(O_3SOH)$, the appreciation of its OD character was not obvious, as its diffraction pattern did not present diffuse reflections or streaks, which are the most relevant features of an OD structure and immediately indicate the direction of missing periodicity of the equivalent layers. In fact, the diffraction pattern appeared to be normal, with Laue symmetry *mmm*, suggesting an orthorhombic structure with cell parameters $a = 15.14$, $b = 8.199$, $c = 10.722$ Å.

However, a careful scrutiny showed the following peculiarities:

(a1) in the layers with $k = 2n$, only the reflections with even l values are present; moreover, the reflections with $k = 2n$ (and $l = 2n$) are generally intense, whereas the reflections with $k = 2n + 1$ are significantly weaker;

(a2) in the rows $00l$, $02l$, ..., only reflections with $l = 4n$ are present;

(b1) in the layer $hk0$, only reflections with $h = 2n$ are present;

(b2) in the layer $h0l$, only reflections with $l = 2n$ are present; this rule is a special case of rule (a1).

Rules (a) are not required by any orthorhombic space group. However, they become ordinary rules for reflections with $k = 2K$ (and thus with $l = 2L$), as considered by themselves. These reflections correspond to a reciprocal lattice with vectors $\mathbf{A}^*$ $\mathbf{B}^*$ $\mathbf{C}^*$ related to the vectors $\mathbf{a}^*$ $\mathbf{b}^*$ $\mathbf{c}^*$, *i. e.*:

$$\mathbf{A}^* = \mathbf{a}^*$$

$$\mathbf{B}^* = 2\mathbf{b}^*$$

$$\mathbf{C}^* = 2\mathbf{c}^*$$

For these family reflections, peculiarities (a) and (b) give the following rules:

$$0KL \text{ present for } L = 2n$$

$$hK0 \text{ present for } h = 2n$$

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(10) Sheldrick, G. M. SHELXTL, Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, WI, 1992.

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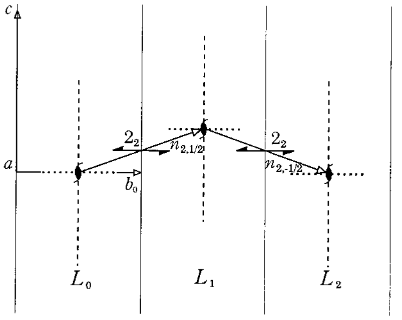

Figure 2. Sequence of layers in the MDO1 polytype. Only the translational components of the σ glide operations are shown.

The possible space groups of the "superposition structure" are *Pc*2*a* or *Pcma*.

Systematic absences not limited to the family reflections are obviously dependent on symmetry operators of the single layer (λ-POs). The systematic absences (b1) point to a layer symmetry:

$$P \;\_\; \_\; a$$

Dornberger-Schiff and Fichtner presented[13] all the "OD groupoid families" in triclinic, monoclinic and orthorhombic systems and indicated how to select the correct groupoid family and to establish the appropriate values of *r*, *s*, and *p* consistent with the peculiarities of the diffraction pattern. By applying their procedure, it was possible to obtain the following OD groupoid family:

$$\begin{array}{cccc} P & 2_1 & (c) & a \\ \{n_{2,1/2} & & (2_2) & 2_{-1/2}\} \end{array}$$

The symbol indicates that layers of symmetry $P2_1ca$ (and periods $a = 15.14$, $c = 10.722$ Å, width $b_0 = b/2 = 4.10$ Å) follow each other along the direction normal to (010). Successive layers may be related through the operation $n_{2,1/2}$ (normal to **a**, with translational component $\mathbf{b}_0 + \mathbf{c}/4$) or by the operation $n_{2,-1/2}$ (normal to **a**, with translational component $\mathbf{b}_0 - \mathbf{c}/4$). Pairs of adjacent layers related by $n_{2,1/2}$ and pairs of adjacent layers related by $n_{2,-1/2}$ are geometrically equivalent. Infinite structures are possible corresponding to the infinite possible sequences of operators $n_{2,1/2}$ and $n_{2,-1/2}$.

Among the ordered structures (polytypes), two are characterized by a homogeneous sequence of the operators: consequently, in those structures (structures of maximum degree of order, MDO), not only pairs, but triples (and quadruples, ..., *n*-uples) of adjacent layers are geometrically equivalent.

MDO1 sequence $n_{2,1/2}/n_{2,-1/2}/n_{2,1/2}/n_{2,-1/2}/.......$

MDO2 sequence $n_{2,1/2}/n_{2,1/2}/n_{2,1/2}/n_{2,1/2}/.......$

(or $n_{2,-1/2}/n_{2,-1/2}/n_{2,-1/2}/n_{2,-1/2}/...$)

In MDO1, the glide $n_{2,1/2}$, followed by $n_{2,-1/2}$, operates as indicated in Figure 2. The layer L_2 returns to the same level as L_0 and the glide *c* (normal to $\mathbf{b}_0$; λ operation of the single layer) is valid for the whole structure. The σ operation 2_2 continues in the subsequent layers, becoming a 2_1 operation totally, with reference to a parameter $b = 2b_0$. The other operators (λ or σ) are not total operators. Therefore, the MDO1 polytype has space group symmetry $P12_1/c1$, with cell parameters

$$\mathbf{a}_1 = \mathbf{a}$$

$$\mathbf{b}_1 = \mathbf{b}$$

$$\mathbf{c}_1 = \mathbf{c}$$

$$\beta = 90°$$

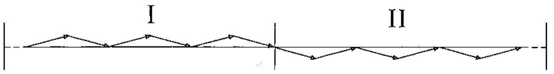

Figure 3. Scheme of the twin relationships as seen down the *a* axis (*c* vertical). Arrows show the translational components of the σ glide operations.

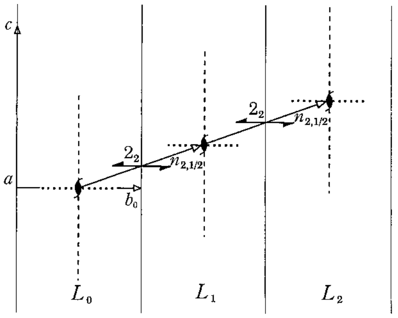

Figure 4. Layer sequence in the MDO2 polytype, with the same conventions as in Figure 2.

We considered that the crystal under study most probably corresponded to the MDO1 polytype. The fact that not only the family reflections but the whole diffraction pattern displayed an orthorhombic symmetry could be explained by twinning. In fact, the occurrence of a stacking fault in the regular sequence of layers gives rise to twinning, with (001) as twinning plane (Figure 3). In Figure 3, I and II are twinning related, due to the OD character of the compound. The occurrence of stacking faults may be frequent, giving rise to polysynthetic twinning with frequent alternations of both twin individuals. It is probable that the twin ratio is 1:1; in this case the twinning plane would add another symmetry plane to the diffraction pattern, giving rise to the diffraction symmetry *mmm*.

As a matter of fact, the structure was easily solved by applying direct methods in the space group $P2_1/c$. The refinement confirmed the (001) twinning with the twin ratio 1:1.

In MDO2, the glide $n_{2,1/2}$, regularly followed by $n_{2,1/2}$, operates as indicated in Figure 4. The layer L_2 does not return to the same level as L_0 and the λ glide *c* is no more valid for the whole structure. On the other hand, the σ operation $n_{2,1/2}$ continues in the succeeding layers, becoming a total *b* glide, with the new cell axes

$$\mathbf{a}_2 = \mathbf{a}$$

$$\mathbf{b}_2 = 2\mathbf{b}_0 - \mathbf{c}/2 = \mathbf{b} - \mathbf{c}/2$$

$$\mathbf{c}_2 = \mathbf{c}$$

$$\alpha = 90° + \arctan(c/2b)$$

The λ operation 2_1, parallel to **a**, is valid for the whole structure. The MDO2 polytype has symmetry $P2_1/b11$ with $a = 15.14$ Å, $b = 9.797$ Å, $c = 10.722$ Å, and $\alpha = 123.18°$.

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[13] Dornberger-Schiff, K.; Fichtner, K. *Krist. Tech.* **1972**, *7*, 1035.

The ordered sequence $n_{2,-1/2}/n_{2,-1/2}/n_{2,-1/2}/n_{2,-1/2}$... corresponds to the twin structure.

Results and Discussion

The hydrogen sulfate of silver(I) has been prepared by treating either silver oxide or silver sulfate with concentrated sulfuric acid, see eq 1 and eq 2, respectively.

$$Ag_2O + H_2SO_4 \rightarrow 2Ag(O_3SOH) + H_2O \qquad (1)$$

$$Ag_2SO_4 + H_2SO_4 \rightarrow 2Ag(O_3SOH) \qquad (2)$$

Due to the high affinity of water for sulfuric acid, moisture can easily revert eq 2 and form silver sulfate. Thus, the reactions must be carried out, and the product must be handled, under an atmosphere rigorously protected from moisture. The synthesis of silver hydrogen sulfate through reaction 2 contrasts with the results reported by some authors[4] who attributed the failure to observe reaction to the low solubility of the sulfate in sulfuric acid. A further complication arises from the difficulty of separating the product from sulfuric acid (bp 370 °C, dec); this problem has been solved by washing the crystalline product with dimethyl sulfate (bp 188 °C, dec; bp_{15} 76 °C), the latter being completely miscible with the former and easily removed in vacuo. Silver hydrogen sulfate can be recrystallized from warm sulfuric acid or from a H_2SO_4/$(MeO)_2SO_2$ mixture giving well-shaped, colorless, tabular crystals, which are stable under a sulfuric acid layer but collapse to a white slurry when exposed to air. Crystals of two different shapes (prismatic or needlelike) were observed, depending on the temperature of crystallization, both having the same structure.

The crystal structure of $Ag(O_3SOH)$ shows an asymmetric unit consisting of four silver cations and four hydrogen sulfate anions, which is a unique feature among the hydrogen sulfates of monovalent cations studied so far.[14] This finding is probably related to the large variety of coordination geometries the silver cation can display in its compounds. By restricting our attention to the silver derivatives with tetrahedral oxoanions, metal coordination ranges from 4 (distorted tetrahedral) in Ag_3AsO_4[15] and Ag_3PO_4[16] with Ag···Ag interactions (3.06 and 2.73 Å, respectively), to 4 + 2 (heavily distorted octahedral) in Ag_2SO_4[17] and Ag_2CrO_4[18] (where an Ag^+ cation is five-coordinate) to 4 + 4 (dodecahedral) in $AgClO_4$.[19] The overall structure of our compound, see Figure 5, consists of planar layers of cations alternating in the *b* direction with layers of anions spaced by *b*/4. Within the layers, both the anions and the cations are disposed following an almost square net with translations of *a*/4 and *c*/2.

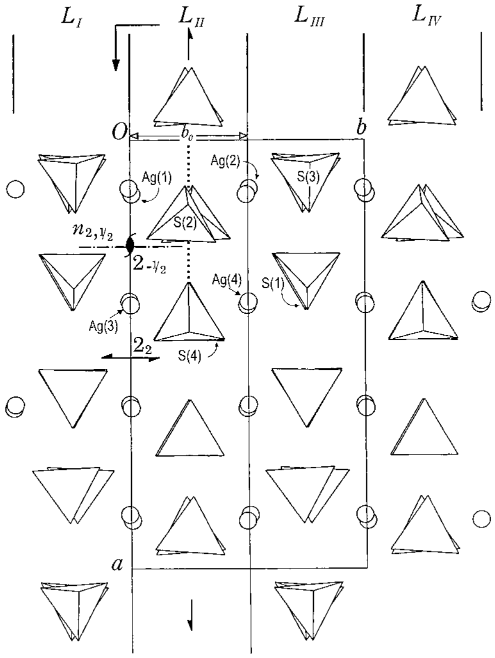

Figure 5. View of the crystal structure of $Ag(O_3SOH)$ along the *c* axis; single-layer operators and operators relating two adjacent layers are indicated. Spheres and tetrahedra represent silver cations and sulfate anions, respectively; hydrogen atoms have been omitted.

The four hydrogen sulfate anions have tetrahedral geometry, slightly distorted toward a trigonal pyramid, due to lengthening of the S−O bond connected to the hydroxyl groups, with a mean length of 1.57 Å, to be compared with the mean value of 1.45 Å observed for the other S−O bonds. A list of S−O bond distances is in Table 3, together with the other bond distances and angles. The reported parameters are in keeping with those found in α- and β-$Na(O_3SOH)$:[14a] in this compound, the mean S−O distances are 1.44 and 1.46 Å, to be compared with 1.52 and 1.58 Å for the S−OH bonds. Moreover, in sulfuric acid itself,[14g] the S−O and S−OH bond distances are 1.426(1) and 1.537(1) Å, respectively, in good agreement with our findings.

In sodium hydrogen sulfate the metal cation, with a radius (1.02 Å) only slightly smaller than that (1.15 Å)

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Table 3. Selected Bond Distances (Å) and Angles (deg) of Ag(O_3SOH)

Ag(1)−O(13^{i})	2.35(2)	Ag(4)−O(42^{xii})	2.53(2)
Ag(1)−O(33^{ii})	2.463(14)	Ag(4)−O(44^{viii})	2.624(12)
Ag(1)−O(23^{iii})	2.494(10)	Ag(4)−O(42^{ix})	2.63(1)
Ag(1)−O(34^{iv})	2.556(14)	Ag(4)−O(11^{ix})	2.644(13)
Ag(1)−O(21^{ii})	2.663(12)	S(1)−O(11)	1.60(2)
Ag(1)−O(32^{v})	2.668(13)	S(1)−O(12)	1.43(2)
Ag(1)···O(22^{ii})	2.84(1)	S(1)−O(13)	1.424(14)
Ag(2)−O(14)	2.44(2)	S(1)−O(14)	1.39(2)
Ag(2)−O(23^{iii})	2.461(10)	S(2)−O(21)	1.557(14)
Ag(2)−O(33^{iv})	2.54(2)	S(2)−O(22)	1.439(14)
Ag(2)−O(34^{vi})	2.554(14)	S(2)−O(23)	1.455(13)
Ag(2)−O(32^{iii})	2.576(13)	S(2)−O(24)	1.490(12)
Ag(2)−O(21^{ii})	2.762(13)	S(3)−O(31)	1.53(2)
Ag(3)−O(24)	2.427(14)	S(3)−O(32)	1.472(14)
Ag(3)−O(43^{vii})	2.49(2)	S(3)−O(33)	1.45(2)
Ag(3)−O(12^{viii})	2.507(13)	S(3)−O(34)	1.44(2)
Ag(3)−O(43^{ix})	2.516(14)	S(4)−O(41)	1.59(2)
Ag(3)−O(44^{viii})	2.555(13)	S(4)−O(42)	1.46(2)
Ag(3)−O(11^{x})	2.699(13)	S(4)−O(43)	1.46(2)
Ag(4)−O(22)	2.42(2)	S(4)−O(44)	1.485(12)
Ag(4)−O(12^{xi})	2.491(12)		

O(13^{i})−Ag(1)−O(21^{ii})	123.4(5)	O(43^{ix})−Ag(3)−O(43^{vii})	78.6(5)
O(13^{i})−Ag(1)−O(23^{iii})	94.7(5)	O(43^{ix})−Ag(3)−O(44^{viii})	88.2(5)
O(13^{i})−Ag(1)−O(32^{v})	87.6(5)	O(43^{vii})−Ag(3)−O(44^{viii})	81.0(6)
O(13^{i})−Ag(1)−O(33^{ii})	117.3(5)	O(11^{ix})−Ag(4)−O(12^{xi})	75.1(4)
O(13^{i})−Ag(1)−O(34^{iv})	158.4(5)	O(11^{ix})−Ag(4)−O(22)	125.0(5)
O(21^{ii})−Ag(1)−O(23^{iii})	74.5(4)	O(11^{ix})−Ag(4)−O(42^{ix})	71.0(4)
O(21^{ii})−Ag(1)−O(32^{v})	148.8(4)	O(11^{ix})−Ag(4)−O(44^{viii})	147.5(5)
O(21^{ii})−Ag(1)−O(33^{ii})	76.3(5)	O(11^{ix})−Ag(4)−O(42^{xii})	75.1(5)
O(21^{ii})−Ag(1)−O(34^{iv})	74.4(5)	O(12^{xi})−Ag(4)−O(22)	97.3(6)
O(23^{iii})−Ag(1)−O(32^{v})	108.5(4)	O(12^{xi})−Ag(4)−O(42^{ix})	141.5(5)
O(23^{iii})−Ag(1)−O(33^{ii})	145.2(5)	O(12^{xi})−Ag(4)−O(44^{viii})	119.2(4)
O(23^{iii})−Ag(1)−O(34^{iv})	77.8(5)	O(12^{xi})−Ag(4)−O(42^{xii})	80.7(6)
O(32^{v})−Ag(1)−O(33^{ii})	87.5(4)	O(22)−Ag(4)−O(42^{ix})	117.0(5)
O(32^{v})−Ag(1)−O(34^{iv})	76.0(5)	O(22)−Ag(4)−O(44^{viii})	84.1(5)
O(33^{ii})−Ag(1)−O(34^{iv})	76.5(5)	O(22)−Ag(4)−O(42^{xii})	158.8(5)
O(14)−Ag(2)−O(21^{ii})	107.2(5)	O(42^{ix})−Ag(4)−O(44^{viii})	83.5(5)
O(14)−Ag(2)−O(23^{iii})	92.9(6)	O(42^{ix})−Ag(4)−O(42^{xii})	73.5(5)
O(14)−Ag(2)−O(32^{iii})	92.2(5)	O(44^{viii})−Ag(4)−O(42^{xii})	78.7(5)
O(14)−Ag(2)−O(33^{iv})	172.1(4)	O(14)−S(1)−O(13)	111.5(12)
O(14)−Ag(2)−O(34^{vi})	112.1(5)	O(14)−S(1)−O(12)	111.9(8)
O(23^{iii})−Ag(2)−O(21^{ii})	73.2(4)	O(13)−S(1)−O(12)	111.6(8)
O(23^{iii})−Ag(2)−O(32^{iii})	127.6(4)	O(14)−S(1)−O(11)	107.7(8)
O(23^{iii})−Ag(2)−O(33^{iv})	82.6(5)	O(13)−S(1)−O(11)	106.3(8)
O(23^{iii})−Ag(2)−O(34^{vi})	139.1(5)	O(12)−S(1)−O(11)	107.7(10)
O(33^{iv})−Ag(2)−O(34^{vi})	75.3(4)	O(22)−S(2)−O(23)	118.1(7)
O(33^{iv})−Ag(2)−O(21^{ii})	77.8(5)	O(22)−S(2)−O(24)	112.3(9)
O(33^{iv})−Ag(2)−O(32^{iii})	85.5(5)	O(23)−S(2)−O(24)	112.7(7)
O(34^{vi})−Ag(2)−O(32^{iii})	84.9(5)	O(22)−S(2)−O(21)	101.2(8)
O(34^{vi})−Ag(2)−O(21^{ii})	68.8(5)	O(23)−S(2)−O(21)	106.1(10)
O(21^{ii})−Ag(2)−O(32^{iii})	151.6(4)	O(24)−S(2)−O(21)	104.5(8)
O(24)−Ag(3)−O(11^{x})	107.6(4)	O(34)−S(3)−O(33)	113.8(11)
O(24)−Ag(3)−O(12^{viii})	85.2(5)	O(34)−S(3)−O(32)	113.4(8)
O(24)−Ag(3)−O(43^{vii})	164.0(4)	O(33)−S(3)−O(32)	111.3(8)
O(24)−Ag(3)−O(43^{ix})	117.3(5)	O(34)−S(3)−O(31)	107.1(9)
O(24)−Ag(3)−O(44^{viii})	97.3(5)	O(33)−S(3)−O(31)	103.4(9)
O(11^{x})−Ag(3)−O(12^{viii})	73.9(4)	O(32)−S(3)−O(31)	107.0(10)
O(11^{x})−Ag(3)−O(43^{vii})	77.5(5)	O(42)−S(4)−O(43)	115.0(12)
O(11^{x})−Ag(3)−O(43^{ix})	72.7(5)	O(42)−S(4)−O(44)	113.1(8)
O(11^{x})−Ag(3)−O(44^{viii})	153.5(5)	O(43)−S(4)−O(44)	110.5(8)
O(12^{viii})−Ag(3)−O(43^{ix})	144.1(5)	O(42)−S(4)−O(41)	107.2(9)
O(12^{viii})−Ag(3)−O(44^{viii})	118.0(4)	O(43)−S(4)−O(41)	105.5(9)
O(12^{viii})−Ag(3)−O(43^{vii})	81.7(6)	O(44)−S(4)−O(41)	104.6(11)

[a] Symmetry transformations used to generate equivalent atoms: i = x, $y - 1$, z; ii = x, $-y + 1/2$, $z - 1/2$; iii = x, y, $z - 1$; iv = $-x$, $-y + 1$, $-z + 1$; v = x, $y - 1$, $z - 1$; vi = x, $-y + 3/2$, $z - 1/2$; vii = $-x + 1$, $-y$, $-z + 1$; viii = x, $-y + 1/2$, $z + 1/2$; ix = x, y, $z + 1$; x = x, $y - 1$, $z + 1$; xi = x, $-y + 3/2$, $z + 1/2$; xii = $-x + 1$, $-y + 1$, $-z + 1$; xiii = $-x + 1$, $y + 1/2$, $-z + 1/2$; xiv = x, $y + 1$, z; xv = $-x$, $-y + 1$, $-z + 2$.

of silver(I),[20] has been described[14a] as hepta- or octacoordinate, the Na−O distances ranging from 2.347(7) to 2.983(7) Å. In the present case, we prefer to describe silver as hexacoordinate, with Ag−O distances ranging between 2.35(2) and 2.76(1) Å. In fact, the sequence of increasing Ag−O bond distances for Ag(2), Ag(3), and Ag(4) presents a gap after the sixth distance, the seventh one being 3.06−3.26 Å; only one of the silver cations, Ag(1), presents a seventh Ag−O distance [2.84(1) Å] only slightly greater than the sixth one [2.67(1) Å].

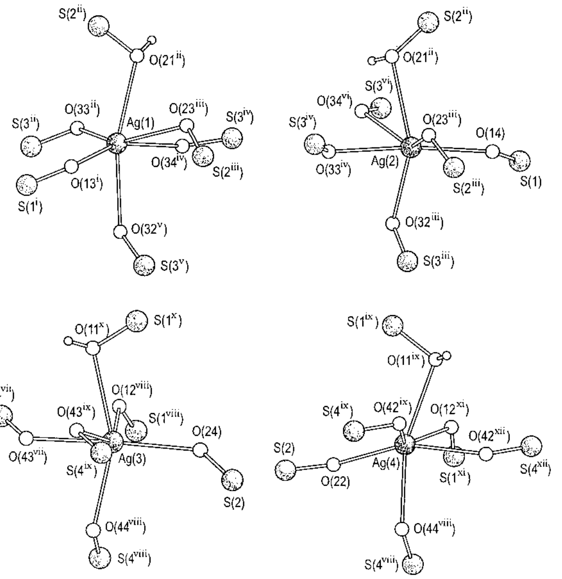

Figure 6. Coordination of the silver cations in Ag(O_3SOH). Atom labeling is the same as in Table 3.

As shown in Figure 6, the coordination geometries around the metal cation can be described as heavily distorted octahedral [for sake of simplicity, we have represented as distorted octahedral also the coordination of Ag(1)]. As shown in the figure, some oxygens are engaged in two bonds with different silver ions, while others link one silver cation only, corresponding changes of bond lengths being as expected. Two hydrogen sulfate OH groups, namely O(31) and O(41), are not linked to any metal ion.

A further contribution to the stability of the structure is given by a network of hydrogen bonds. Strong interactions are observed between the hydrogen sulfates (1) and (4), the O(11)···O(44^{xiii}) and O(41)···O(14) distances being 2.67(2) and 3.04(2) Å, respectively (see footnote of Table 3 for atom labeling), and between hydrogen sulfates (3) and (2), the O(31)···O(24^{xiv}) distance being 2.68(2) Å. Hydrogen sulfate (2) behaves as a hydrogen donor toward two different oxygen atoms, the O(21)···O(32^{xv}) and O(21)···O(34^{i}) distances being 2.68(2) and 3.01(2) Å, respectively.

Conclusions

Depending on the crystallization procedure and on the composition of the solution, the crystals of Ag(O_3SOH) are tabular or needlelike. Both, however, are twinned with twins present in the same amount and displaying the same diffraction pattern. The systematic absences, incompatible with any space group, can be attributed to the OD character of the compound. The OD approach allowed the structure to be solved, which was shown to correspond to one of the two main polytypes of a whole family of possible OD structures. The structure of the other main polytype could be anticipated, but we have

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(20) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

not been able to observe it among the crystals we have studied.

As a matter of fact, the polytype presents a structure showing a considerable desymmetrization with respect to the ideal symmetry of the single layer and, as it can be seen in Figure 5, the $P2_1ca$ layer symmetry is only approximately valid for this structure. It is conceivable that this polytype is stabilized through desymmetrization, thus explaining our failure to find other possible phases of the same OD family.

Silver hydrogen sulfate has an interesting chemistry in solution too. This paper shows that solutions of the title compound, contrary to an earlier report,[4] can be prepared from Ag_2SO_4 and concentrated sulfuric acid. Solutions of $Ag(O_3SOH)$ in concentrated sulfuric acid absorb carbon monoxide reversibly up to a CO/Ag molar ratio of 0.12 at 28 °C. The present results show that the earlier carbonylation experiments by Manchot and König[7a] (Ag_2SO_4 in sulfuric acid under CO) and by Souma[7b] and co-workers (Ag_2O in sulfuric acid under CO), both involve silver(I) hydrogen sulfate. No absorption of carbon monoxide was observed for silver hydrogen sulfate in the solid state: this is hardly surprising since coordination of CO to silver would require a considerable structural rearrangement and the cleavage of the silver−oxygen bonds. Up to now, the only crystallographically established[21] uncharged carbonyl derivative of silver(I) is $Ag(CO)(OTeF_5)_2B(OTeF_5)_2$ synthesized by Strauss et al., where the silver cation is three-coordinate. On the other hand, it is interesting that the electron-withdrawing power of the oxygen-ligated proton in silver(I) hydrogen sulfate is sufficiently strong to somewhat stabilize the Ag−CO bond in solution. Work is in progress aimed at studying the effect of temperature and sulfuric acid concentration on the carbonylation of silver(I) in solution.

We further point out that this paper has established the possibility of obtaining a hydrogen sulfate derivative by using the metal oxide/sulfuric acid route: this method of preparation will be extended to other oxides of transition metals, to verify its generality and thus possibly explore a completely new class of compounds, whose proton mobility might be modulated by both the nature of the cation and its oxidation state.

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Supporting Information Available: Anisotropic displacement parameters and hydrogen coordinates (1 page) and structure factors (5 pages). Ordering information is given on any current masthead page. Further details of the crystal structure determination can be ordered from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, under the depository number CSD-407979.

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