

Reactor Centrum Nederland, Petten, for performing the neutron-diffraction experiment and the profile refinement.

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The Crystal and Molecular Structure of Ethylenebis(biguanide)silver(III) Sulphate Hydrogen Sulphate Monohydrate [Ag(C₆H₁₆N₁₀)]SO₄HSO₄·H₂O

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Crystals of the title compound are triclinic (*P* $\bar{1}$) with unit-cell dimensions $a=8.645$, $b=9.177$, $c=13.363$ Å, $\alpha=104.2$, $\beta=117.5$, $\gamma=99.4^\circ$, $Z=2$. The X-ray analysis carried out with diffractometer data (Mo $K\alpha$ radiation; final $R=4.0\%$ for 2875 independent reflexions) shows that the organic molecule behaves as a tetradentate ligand. It chelates to metal in a nearly planar arrangement giving rise to complex cations in which silver is in the oxidation state III. In a *trans* arrangement with respect to the coordination plane there are SO₄²⁻ and HSO₄⁻ ions, each of which directs an oxygen atom towards the metal. These two Ag–O interactions are rather long (2.932, 2.944 Å) so the complete coordination polyhedron is an elongated square bipyramid. The water molecule is involved in a system of hydrogen bonds involving sulphate oxygen and ethylenebis(biguanide) nitrogen atoms. A strong hydrogen bond (2.51 Å) is also observed between the HSO₄⁻ and SO₄²⁻ anions.

Introduction

Ethylenebis(biguanide) is an interesting coordinating ligand containing nitrogens as donor atoms, which is able to stabilize the oxidation state III in silver (Rây & Chakravarty, 1944).

From the crystal structures of metal complexes with ethylenebis(biguanide) (hereinafter called EBG) studied so far [Cu(EBG)Cl₂·H₂O (Kunchur & Mathew, 1966; Mathew & Kunchur, 1970); Ni(EBG)Cl₂·H₂O (Coghi, Mangia, Nardelli & Pelizzi, 1969; Holian & Marsh, 1970; Ward, Caughlan & Smith, 1971); Ag(EBG)(NO₃)₃ (Kunchur, 1968)] it was deduced that the ligand chelates to metal in a planar fashion through four nitrogen atoms: coordination is perfectly planar for the Cu and Ni derivatives and slightly distorted for the Ag derivative. This distortion is also observed in the title compound, which is particularly interesting because it contains both SO₄²⁻ and HSO₄⁻ ions.

Experimental

A solution of silver sulphate (0.3 g) in water was added to a solution of ethylenebis(biguanidinium) hydrogen

sulphate (1 g) prepared as described by Chakravarty & Rây (1944). The resulting mixture, cooled to 10°C, was oxidized by an aqueous solution of potassium peroxodisulphate (1 g) and kept at 10°C for 12 h until red-orange silky diamagnetic crystals separated. These crystals were recrystallized from hot dilute sulphuric acid.

Analysis for C₆H₁₉AgN₁₀O₉S₂: calculated C=13.2, H=3.5, Ag=19.8, N=25.7%; found C=12.9, H=4.2, Ag=19.6, N=25.3%.

The lattice parameters were first determined from rotation and Weissenberg photographs and then refined from a least-squares fit of $(\theta, \chi, \varphi)_{hkl}$ angles measured by single-crystal diffractometry for 20 reflexions. The most significant crystal data are quoted in Table 1. All the diffraction measurements were made at room-temperature on a prismatic crystal with a mean diameter of 0.064 mm, using an automated on-line Siemens AED single-crystal diffractometer with Mo $K\alpha$ radiation ($\lambda=0.7107$ Å). Of the 3948 independent reflexions which were examined within the range $0 < 2\theta < 55^\circ$, 2875 had an intensity greater than twice the standard deviation of the intensity; the remaining 1073 reflexions were coded as unobserved and

were not included in the refinement. A standard reflexion was periodically measured after 20 reflexions to check the stability of the instrument and of the sample. The intensity data were reduced to structure amplitudes by application of Lorentz and polarization factors. No correction was made for absorption as this was considered negligible ($\mu r = 0.05$). The absolute scale was obtained by correlating observed and calculated values.

Table 1. *Crystallographic data*

$\text{C}_6\text{H}_{17}\text{AgN}_{10}\text{O}_8\text{S}_2 \cdot \text{H}_2\text{O}$; F.W. 547.3. Triclinic; space group $P\bar{1}$;
 $a = 8.645 \pm 5$, $b = 9.177 \pm 5$, $c = 13.363 \pm 6$ Å;
 $\alpha = 104.2 \pm 2$, $\beta = 117.5 \pm 2$, $\gamma = 99.4 \pm 2^\circ$;
 $U = 863.1$ Å³, $Z = 2$, $D_m = 1.96$, $D_x = 2.11$ g cm⁻³;
 $\mu(\text{Mo K}\alpha) = 14.5$ cm⁻¹; $F(000) = 552$

Structure determination and refinement

The structure was solved by the heavy-atom technique, starting from the Patterson coordinates for Ag. All the non-hydrogen atoms were located from the first silver-phased Fourier synthesis. Four cycles of block-diagonal least-squares refinement [the quantity minimized was $\sum w(\Delta|F_{\text{meas}}|)^2$ with unit weights] with isotropic thermal parameters improved the conventional R index [$\sum \Delta F_{\text{meas}} / \sum F_{\text{meas}}$] from 21.3 to 8.7% and this last value further dropped to 4.5% after six cycles with anisotropic thermal parameters. A difference map was computed at this stage and yielded the positions of all 19 hydrogen atoms. The final R , after isotropic refinement of the hydrogen atoms, is 4.0%.

Table 2. *Final atomic fractional coordinates ($\times 10^4$) and thermal parameters (Å²), with estimated standard deviations, for non-hydrogen atoms*

Anisotropic thermal parameters are in the form: $\exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

| | x/a | y/b | z/c | B_{11} | B_{22} | B_{33} | B_{12} | B_{13} | B_{23} |
|-------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|
| Ag | 183 (1) | 29 (1) | 2715 (0) | 1.72 (1) | 1.74 (1) | 1.79 (1) | 0.39 (1) | 1.12 (1) | 0.33 (1) |
| S(1) | -2505 (2) | 2941 (2) | 1497 (1) | 2.14 (5) | 1.55 (5) | 1.94 (5) | 0.34 (4) | 1.39 (4) | 0.43 (4) |
| S(2) | 2804 (2) | -3146 (2) | 3386 (1) | 1.41 (4) | 1.97 (5) | 1.85 (5) | 0.26 (4) | 0.91 (4) | 0.39 (4) |
| O(1) | -853 (6) | 3927 (5) | 2807 (4) | 2.5 (2) | 3.3 (2) | 2.5 (2) | -0.3 (1) | 1.5 (1) | 0.0 (1) |
| O(2) | -2626 (7) | 1301 (5) | 1302 (4) | 5.2 (2) | 2.1 (2) | 3.1 (2) | 1.1 (2) | 2.4 (2) | 1.1 (1) |
| O(3) | -4054 (6) | 3305 (5) | 1497 (4) | 3.0 (2) | 3.8 (2) | 3.5 (2) | 1.0 (2) | 2.3 (2) | 1.1 (2) |
| O(4) | -2083 (6) | 3469 (5) | 682 (4) | 3.9 (2) | 2.3 (2) | 2.9 (2) | 1.1 (1) | 2.6 (2) | 1.2 (1) |
| O(5) | 4467 (6) | -2525 (6) | 4602 (4) | 2.2 (2) | 5.0 (2) | 2.7 (2) | 0.7 (2) | 1.0 (1) | 1.5 (2) |
| O(6) | 3197 (6) | -2718 (5) | 2534 (4) | 3.1 (2) | 3.4 (2) | 2.7 (2) | 0.5 (2) | 1.9 (2) | 0.8 (1) |
| O(7) | 1380 (6) | -2546 (5) | 3466 (4) | 2.8 (2) | 3.3 (2) | 2.8 (2) | 1.1 (1) | 1.9 (2) | 0.9 (1) |
| O(8) | 2131 (6) | -4903 (5) | 2971 (5) | 2.9 (2) | 2.4 (2) | 6.6 (2) | 0.7 (1) | 3.1 (2) | 1.3 (2) |
| O(9) | 4901 (6) | 3770 (5) | 3604 (4) | 3.0 (2) | 3.0 (2) | 4.0 (2) | 1.1 (2) | 1.8 (2) | 1.3 (2) |
| N(1) | -1279 (6) | -1893 (5) | 1219 (4) | 1.7 (2) | 1.5 (2) | 1.6 (2) | 0.1 (1) | 1.0 (1) | 0.3 (1) |
| N(2) | -1510 (7) | -3963 (5) | -295 (5) | 3.6 (2) | 1.7 (2) | 3.2 (2) | 0.2 (2) | 2.6 (2) | -0.1 (2) |
| N(3) | 708 (6) | -1594 (5) | 476 (4) | 2.0 (2) | 2.0 (2) | 1.6 (2) | 0.5 (1) | 1.3 (1) | 0.3 (1) |
| N(4) | 3167 (6) | 442 (6) | 1019 (4) | 2.5 (2) | 2.7 (2) | 2.7 (2) | 0.3 (2) | 1.9 (2) | 0.7 (2) |
| N(5) | 2008 (6) | 618 (5) | 2264 (4) | 2.2 (2) | 2.2 (2) | 2.2 (2) | 0.0 (1) | 1.6 (2) | 0.0 (1) |
| N(6) | 1565 (6) | 1854 (5) | 4261 (4) | 1.4 (2) | 2.4 (2) | 2.1 (2) | -0.3 (1) | 1.1 (1) | -0.6 (1) |
| N(7) | 1962 (7) | 3734 (6) | 5941 (4) | 2.7 (2) | 2.6 (2) | 2.5 (2) | -0.2 (2) | 1.8 (2) | -0.2 (2) |
| N(8) | -815 (6) | 1775 (5) | 4656 (4) | 1.9 (2) | 2.3 (2) | 1.6 (2) | 0.4 (1) | 1.2 (1) | 0.1 (1) |
| N(9) | -3710 (6) | 100 (6) | 3729 (4) | 2.1 (2) | 2.6 (2) | 2.4 (2) | 0.2 (2) | 1.7 (2) | 0.0 (2) |
| N(10) | -1836 (6) | -593 (5) | 3010 (4) | 1.6 (2) | 2.0 (2) | 1.5 (2) | 0.1 (1) | 1.0 (1) | 0.3 (1) |
| C(1) | -711 (7) | -2489 (6) | 501 (4) | 1.7 (2) | 1.7 (2) | 1.7 (2) | 0.5 (1) | 1.0 (2) | 0.6 (1) |
| C(2) | 1965 (7) | -130 (6) | 1288 (5) | 2.0 (2) | 1.9 (2) | 1.9 (2) | 0.9 (2) | 1.2 (2) | 0.9 (2) |
| C(3) | 940 (7) | 2437 (6) | 4931 (5) | 2.0 (2) | 1.9 (2) | 1.8 (2) | 0.5 (2) | 1.1 (2) | 0.5 (2) |
| C(4) | -2127 (7) | 385 (6) | 3754 (4) | 1.9 (2) | 2.0 (2) | 1.9 (2) | 0.9 (2) | 1.2 (2) | 0.9 (2) |
| C(5) | -3416 (7) | -1885 (6) | 1913 (5) | 1.7 (2) | 2.4 (2) | 2.2 (2) | 0.4 (2) | 1.3 (2) | 0.4 (2) |
| C(6) | -2717 (7) | -2909 (6) | 1274 (5) | 2.0 (2) | 1.9 (2) | 2.2 (2) | 0.3 (2) | 1.4 (2) | 0.5 (2) |

Final coordinates and thermal parameters with their standard deviations are listed in Tables 2 and 3.* The

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30612 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

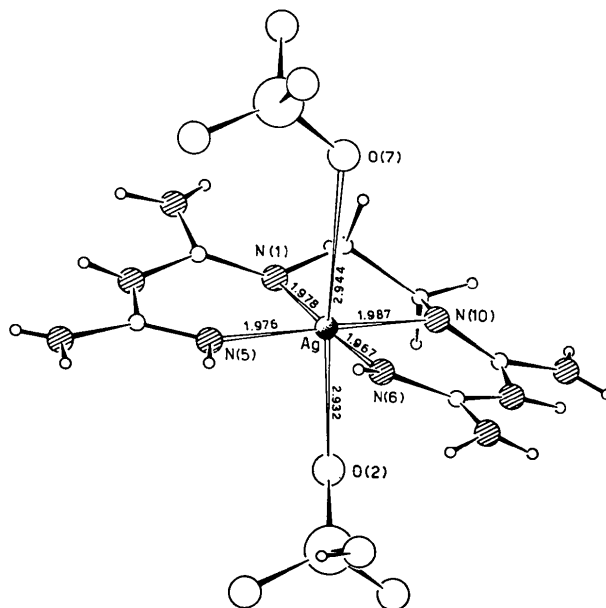


Fig. 1. Clinographic projection of the structure with interatomic distances in the coordination polyhedron.

atomic scattering factors are those of Cromer & Mann (1968) for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for hydrogen atoms.

Table 3. Final atomic fractional coordinates ($\times 10^3$) and isotropic thermal parameters (\AA^2), with estimated standard deviations, for hydrogen atoms

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> |
|-------|------------|------------|------------|----------|
| H(1) | -216 (10) | -446 (9) | -27 (7) | 5 (2) |
| H(2) | -128 (9) | -429 (8) | -86 (6) | 4 (1) |
| H(3) | 108 (10) | -198 (9) | 6 (7) | 5 (2) |
| H(4) | 309 (9) | -1 (8) | 38 (6) | 3 (1) |
| H(5) | 379 (9) | 121 (7) | 144 (6) | 3 (1) |
| H(6) | 257 (9) | 129 (8) | 260 (6) | 4 (1) |
| H(7) | 256 (9) | 219 (8) | 453 (6) | 4 (1) |
| H(8) | 280 (9) | 433 (8) | 594 (6) | 3 (1) |
| H(9) | 151 (9) | 416 (8) | 631 (6) | 3 (1) |
| H(10) | -98 (8) | 214 (7) | 521 (5) | 2 (1) |
| H(11) | -364 (9) | 74 (8) | 432 (6) | 3 (1) |
| H(12) | -445 (9) | -64 (7) | 334 (6) | 3 (1) |
| H(13) | -409 (8) | -137 (7) | 152 (5) | 3 (1) |
| H(14) | -412 (9) | -226 (8) | 218 (6) | 4 (1) |
| H(15) | -222 (8) | -345 (7) | 175 (5) | 3 (1) |
| H(16) | -370 (8) | -351 (7) | 50 (6) | 3 (1) |
| H(17) | -9 (11) | 421 (10) | 275 (8) | 6 (2) |
| H(18) | 403 (11) | 429 (10) | 338 (8) | 6 (2) |
| H(19) | 544 (12) | 366 (10) | 452 (8) | 7 (2) |

All calculations were carried out by means of the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

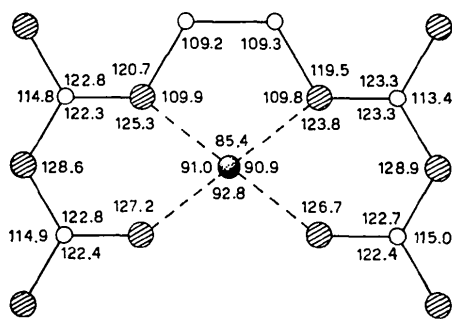
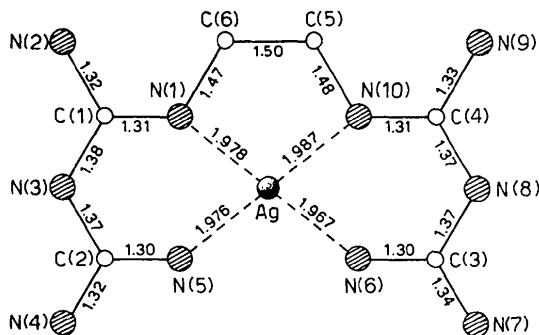


Fig. 2. Bond distances and angles in the cation $[\text{Ag}(\text{C}_6\text{H}_{16}\text{N}_{10})]^{3+}$. The ranges of the e.s.d.'s are 0.006–0.010 Å and 0.2–0.6°, respectively.

Results and discussion

A clinographic projection of the coordination polyhedron is illustrated in Fig. 1 together with the interatomic distances involving the silver atom. As already observed for the other ethylenebis(biguanide) complexes whose structures are known the organic ligand acts as a tetradentate ligand through four nitrogen atoms, wrapping itself around the metal atom. In the present compound the four nitrogens coordinate to silver in a slightly distorted square-planar configuration. These atoms are not strictly coplanar as they show the following deviations from the mean plane through them: N(1) -0.05 , N(5) $+0.06$, N(6) -0.06 , N(10) $+0.05$ Å; Ag is displaced from this plane by only 0.02 Å. The four Ag–N bond distances are all equal within the experimental errors (1.978, 1.976, 1.967, 1.987 Å) and are very close to those found in $\text{Ag}(\text{EBG})(\text{NO}_3)_3$ (Kunchur, 1968) (1.98, 1.98, 2.01, 2.03 Å). Coordination around silver is completed by two oxygen atoms belonging to SO_4^{2-} and HSO_4^- groups, which are on opposite sides with respect to the square plane at rather long distances (2.932, 2.944 Å) so that the whole polyhedron appears as an elongated bipyramid. These two O–Ag bonds are equally tilted with respect to the equatorial plane (75.2 and 75.6° respectively) with O–Ag–O (152.5°) departing significantly from linearity.

Silver is in the unusual oxidation state III, in agreement with the diamagnetic character of the compound and with the observed distribution of the hydrogen atoms.

As a consequence of chelation one five-membered $[\text{AgN}(1)\text{C}(6)\text{C}(5)\text{N}(10): \text{I}]$ and two six membered $[\text{AgN}(1)\text{C}(1)\text{N}(3)\text{C}(2)\text{N}(5): \text{II}; \text{AgN}(6)\text{C}(3)\text{N}(8)\text{C}(4)\text{N}(10): \text{III}]$ rings are formed. Such chelation is common to all the three aforementioned EBG complexes; the only difference concerns the planarity of these rings: none of these is planar in the two Ag complexes, while all three rings are planar in the Ni and Cu complexes. In the present compound the dihedral angle between the mean planes I and II is 6.5°, between I and III 3.3°, and between II and III 9.3°.

Bond distances and angles in the organic molecule are given in Fig. 2. The cation shows a pseudosymmetry C_2 , with the twofold axis passing through Ag and the midpoint of the C(5)–C(6) bond. The distances N(sp^2)–C(sp^2) are not all equal and can be classified in three different groups: the shorter ones (1.31, 1.30, 1.30, 1.31 Å) include the nitrogen atoms involved in coordination to silver, the medium ones (1.32, 1.32, 1.34, 1.33 Å) involve the nitrogen atoms of the NH_2 groups, and the longer ones (1.38, 1.37, 1.37, 1.37 Å) involve the nitrogen atoms of the $>\text{NH}$ groups. All these values indicate some π delocalization, being intermediate between single and double bonds (expected values 1.44 and 1.27 Å respectively).

One interesting feature of the present compound is the presence of two different kinds of sulphate group, one of which is protonated. Table 4 lists bond distances

and angles for these groups. As frequently observed in sulphate compounds (Mootz & Wunderlich, 1970 and references therein), the S-O distance involving the protonated oxygen, S-O(1)=1.554 Å, is significantly longer than the others (average 1.456 Å) and consequently the angles involving that oxygen (average 105.8°) are smaller than the others (average 110.6°).

Table 4. Bond distances (Å) and angles (°) in the sulphate groups

| | | | |
|----------------|-----------|----------------|-----------|
| S(1)-O(1) | 1.554 (8) | S(2)-O(5) | 1.467 (7) |
| S(1)-O(2) | 1.441 (5) | S(2)-O(6) | 1.448 (6) |
| S(1)-O(3) | 1.432 (6) | S(2)-O(7) | 1.464 (6) |
| S(1)-O(4) | 1.457 (6) | S(2)-O(8) | 1.484 (6) |
| O(1)-S(1)-O(2) | 106.6 (3) | O(5)-S(2)-O(6) | 110.9 (3) |
| O(1)-S(1)-O(3) | 104.3 (3) | O(5)-S(2)-O(7) | 108.4 (3) |
| O(1)-S(1)-O(4) | 106.9 (3) | O(5)-S(2)-O(8) | 108.7 (3) |
| O(2)-S(1)-O(3) | 113.6 (3) | O(6)-S(2)-O(7) | 112.0 (3) |
| O(2)-S(1)-O(4) | 111.4 (3) | O(6)-S(2)-O(8) | 108.7 (3) |
| O(3)-S(1)-O(4) | 113.3 (3) | O(7)-S(2)-O(8) | 108.0 (3) |

Fig. 3 shows that the crystal cohesion is governed by an intricate three-dimensional network of hydrogen bonds involving the EBG moiety, the sulphate groups and the water molecule. In particular the hydrogen atom bound to O(1) is involved in a strong hydrogen bond with an oxygen atom belonging to an adjacent SO_4^{2-} group: O(1)-H(17)···O(8) ($x, 1+y, z$)=2.51 Å; O(1)-H(17)-O(8)=168°. The water molecule is involved in four hydrogen bonds; two of these have sulphate oxygens as acceptor atoms: O(9)-H(18)···O(8) ($x, 1+y, z$)=2.74 Å; O(9)-H(18)-O(8)=171°; O(9)-H(19)···O(5) ($1-x, \bar{y}, 1-z$)=2.77 Å; O(9)-H(19)-O(5)=151°, the other two involve ethylenebis(biguanide) nitrogens as donor atoms: O(9)···H(6)-N(5)=2.96 Å, O(9)-H(6)-N(5)=168°; O(9)···H(8)-N(7) ($1-x, 1-y, 1-z$)=2.96 Å, O(9)-H(8)-N(7)=165°.

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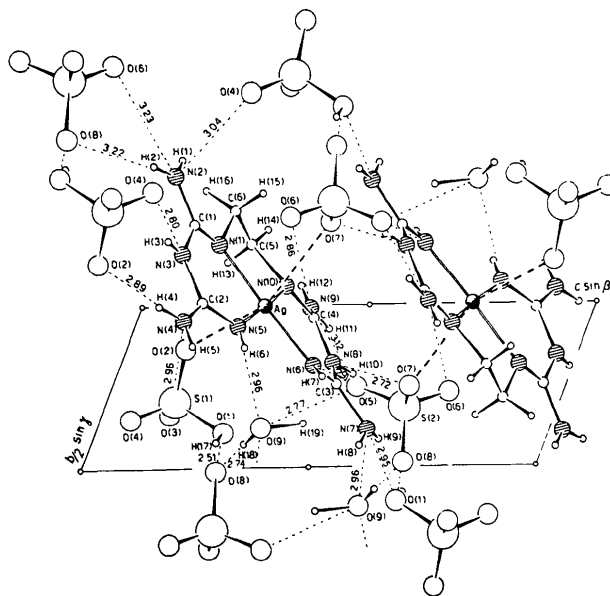


Fig. 3. Diagrammatic projection of the structure, on a plane perpendicular to [100], showing crystal packing and hydrogen bonding.

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