Crystal and Molecular Structure of (*cyclo*-L-Methionylglycine)silver(I) Nitrate †

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The structure of the title compound has been determined by single-crystal *X*-ray diffraction methods. The compound crystallizes in the monoclinic system, space group $P2_1$, with unit-cell dimensions a = 13.634(6), b = 6.225(4), c = 6.784(4) Å, β = 104.8(7)°, and Z = 2. The structure was solved by the heavy-atom method and refined by least-squares calculations to a conventional R factor of 0.052 based on 1 342 independent observed reflections. The structure comprises infinite linear arrays of silver atoms doubly bridged by methionine sulphur atoms and nitrate groups. Each silver atom is surrounded by two sulphurs at 2.511(2) and 2.577(2) Å, two oxygens of a nitrate group at 2.512(7) and 2.574(9) Å, and two oxygens of a second nitrate group at 2.523(9) and 2.855(9) Å. Comparison with the crystal structure of the uncomplexed dipeptide shows remarkable conformational changes upon co-ordination.

Studies on the complexation of a series of metal ions with *cyclo*-L-methionyl-L-methionine and *cyclo*-L-methionylglycine have been reported previously.[1,2] Spectroscopic data show that the methionine sulphur is the primary co-ordination site of these dipeptides, while in some cases there is evidence of additional co-ordination through deprotonated amide nitrogens. This paper describes the crystal and molecular structure of a 1 : 1 complex of *cyclo*-L-methionylglycine and silver nitrate.

Experimental

Suitable crystals of the complex were obtained by slow evaporation of an aqueous solution of the dipeptide and $AgNO_3$ in a 1 : 1 mol ratio. A well formed prismatic crystal of dimensions *ca.* 0.1 × 0.25 × 0.1 mm was mounted on a Philips PW 1100 diffractometer to determine the cell dimensions and to measure the intensity data.

Crystal Data.—$C_7H_{12}AgN_3O_5S$, $M = 358$, Monoclinic, space group $P2_1$, $a = 13.634(6)$, $b = 6.225(4)$, $c = 6.784(4)$ Å, $\beta = 104.8(7)°$, $U = 556.56$ Å^3, $D_m = 2.13$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 2.135$, $F(000) = 356$, λ(Mo-K_α) = 0.7107 Å, $\mu = 2$ cm^{-1}.

Data Collection.—Data, up to $\theta = 28°$, were collected by the $\theta = 2\theta$ step-scan method using Mo-K_α monochromatized radiation. Reflections with $I > 3\sigma(I)$ were considered as observed (1 342 out of 1 454). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination and Refinement of the Structure.—The positions of the silver and sulphur atoms were obtained from a three-dimensional Patterson summation. The remaining non-hydrogen atoms were located in a subsequent electron-density map. The positional and anisotropic thermal parameters for all non-hydrogen atoms were refined to a conventional R factor of 0.052 using block-diagonal least squares. The function minimized was $\Sigma w \Delta F^2$, with $w = 1/[\sigma^2(F) + 0.007F^2]$. Hydrogen atoms were found in a Fourier-difference map, but not refined. Scattering factors for C, H, O, N, and S atoms were those incorporated in the program SHELX;[3] values for the Ag atom with anomalous-dispersion corrections were taken from ref. 4. The absolute configuration was assumed to be that of L-methionylglycine.

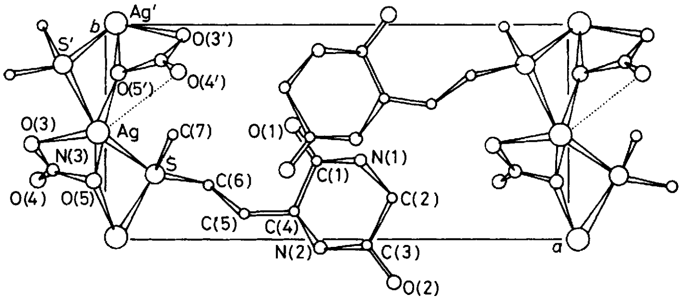

Figure. View of the structure of the complex down the *c* axis, showing the atom-labelling scheme

Results and Discussion

The atomic positional parameters are listed in Table 1, bond lengths and angles in Table 2. A view of the crystal structure down the *c* axis is shown in the Figure. The structure comprises infinite linear arrays of silver atoms doubly bridged by methionine sulphur atoms and nitrate groups. The Ag–(S, NO_3) chains extend in the [010] direction and form layers parallel to the (100) plane, sandwiched between layers containing the cyclic dipeptide. Similar chain and layer arrangements have been found previously in other complexes containing $AgNO_3$.[5]

Each silver atom is surrounded by two sulphur atoms, two oxygen atoms of a nitrate group, and two oxygen atoms of a second nitrate group (see Figure). No other significant metal–ligand contacts are observed. If the O(4') atom is not included in the co-ordination sphere, the silver atom can be regarded as five-co-ordinate. The configuration about the metal, however, does not correspond to any regular form. The $Ag \cdots Ag'$ distance in the chains is 4.25 Å.

Nitrate co-ordination has been found to be bidentate (sym-

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† *catena*-μ-[3-(2'-Methylthioethyl)piperazine-2,5-dione-*S*]-μ-nitrato-*OO'* : *O'O''*-silver(I).

Supplementary data available (No. SUP 23483, 11 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates for non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ag	−0.018 4(1)	0.5000	0.779 7(1)	N(3)	−0.117 4(6)	0.326 9(14)	0.375 6(11)
S(1)	0.103 8(1)	0.292 1(3)	0.052 7(3)	C(1)	0.451 3(6)	0.367 8(12)	0.192 9(11)
O(1)	0.400 6(5)	0.530 5(11)	0.141 2(11)	C(2)	0.614 0(7)	0.194 7(16)	0.356 4(14)
O(2)	0.613 5(5)	−0.183 2(9)	0.382 3(9)	C(3)	0.564 7(6)	−0.022 8(15)	0.319 7(11)
O(3)	−0.163 3(5)	0.439 8(14)	0.471 0(12)	C(4)	0.406 3(5)	0.148 9(13)	0.115 5(11)
O(4)	−0.154 5(8)	0.266 3(18)	0.198 7(12)	C(5)	0.298 5(6)	0.124 3(15)	0.141 3(12)
O(5)	−0.026 4(5)	0.270 3(15)	0.460 4(12)	C(6)	0.221 8(6)	0.255 1(23)	−0.022 4(12)
N(1)	0.547 8(5)	0.372 2(11)	0.302 7(10)	C(7)	0.145 2(6)	0.486 4(24)	0.252 9(14)
N(2)	0.467 1(5)	−0.030 6(11)	0.214 9(11)				

Table 2. Bond distances (Å) and angles (°) with standard deviations in parentheses *

(*a*) Co-ordination sphere

Ag-S	2.511(2)	Ag-S′	2.577(2)	Ag-O(3)	2.512(7)
Ag-O(5)	2.574(9)	Ag-O(5′)	2.523(9)	Ag-O(4′)	2.855(9)

S-Ag-S′	109.2(0.1)	S′-Ag-O(3)	97.2(0.2)
S′-Ag-O(5)	146.8(0.2)	S′-Ag-O(5′)	91.5(0.2)
S-Ag-O(3)	140.4(0.3)	S-Ag-O(5)	102.2(0.2)
S-Ag-O(5′)	126.5(0.2)	O(3)-Ag-O(5)	50.3(0.2)
O(3)-Ag-O(5′)	80.2(0.3)	O(5)-Ag-O(5′)	78.0(0.3)

(*b*) Nitrate

N(3)-O(3)	1.230(12)	N(3)-O(4)	1.226(11)
N(3)-O(5)	1.277(10)		

O(3)-N(3)-O(4)	123.3(0.9)	O(3)-N(3)-O(5)	119.2(0.7)
O(4)-N(3)-O(5)	117.5(0.9)		

(*c*) Ligand

C(1)-N(1)	1.336(10)	O(2)-C(3)	1.215(10)
C(3)-N(2)	1.339(9)	C(6)-S	1.820(9)
O(1)-C(1)	1.226(10)	C(2)-C(3)	1.504(13)
C(5)-C(6)	1.548(11)	C(4)-C(1)	1.531(11)
N(1)-C(2)	1.414(12)	C(4)-C(5)	1.532(11)
N(2)-C(4)	1.451(10)	S-C(7)	1.798(12)

C(1)-N(1)-C(2)	126.9(0.7)	N(1)-C(2)-C(3)	115.6(0.7)
C(2)-C(3)-N(2)	117.5(0.7)	C(3)-N(2)-C(4)	126.2(0.7)
N(2)-C(4)-C(1)	113.3(0.5)	C(4)-C(1)-N(1)	117.4(0.7)
O(1)-C(1)-N(1)	123.1(0.7)	O(1)-C(1)-C(4)	119.3(0.6)
O(2)-C(3)-C(2)	120.1(0.7)	O(2)-C(3)-N(2)	122.4(0.8)
C(1)-C(4)-C(5)	111.2(0.7)	N(2)-C(4)-C(5)	108.7(0.7)
C(4)-C(5)-C(6)	111.0(0.7)	C(5)-C(6)-S	110.4(0.6)
C(6)-S-C(7)	99.7(0.4)		

* Primed symbols represent atoms at the equivalent position $-x, \frac{1}{2} + y, 1 - z$.

metric or asymmetric), unidentate, or bridging.[6] In the case of silver(I) all these binding modes have been observed, the nitrate ion often being involved in more than one type of co-ordination.[5] In the title compound the Ag-O(3), Ag-O(5), and Ag-O(5′) bond lengths are somewhat greater than the sum of ionic radii of silver and oxygen (2.46 Å),[7] whereas the Ag-O-(4′) bond is significantly longer. Therefore, the nitrate group can be considered symmetrically bidentate and bridging, rather than doubly bidentate. The planarity of the NO_3 group is strictly maintained ($\sigma = 0.003$ Å). The Ag atom lies 0.25 Å from the least squares plane through the nitrate atoms O(3), O(4), O(5), and N(3), and 0.37 Å from the plane O(3′), O(4′), O(5′), N(3′).

The Ag-S bond lengths in the complex are consistent with strong metal-ligand binding. In silver(I) complexes Ag-S bond lengths have been found to depend on the co-ordination number of both silver and sulphur, high co-ordination numbers of the metal (four or five) being associated with bond distances from 2.5 to 3.0 Å.[8] The sum of the covalent tetrahedral radii of silver and sulphur is 2.56 Å.[9] The bond angles about the methionine sulphur span the range 101—124° (mean 109°). The C(6)-S-C(7) angle has the same value as in the uncomplexed ligand in the solid state.[2] Structures of thioether complexes containing bridging sulphur atoms have been reported for other metals.[10]

The crystal structure of the uncomplexed ligand [2] displays a nearly planar diketopiperazine ring, the largest internal torsion angle being 3° and the angle between the least-squares planes of the peptide bonds, β,[11,12] close to zero (1.7°). The methionine side chain is folded on this ring, the S atom making an intramolecular contact of 3.25 Å with the neighbouring carbonyl C atom. This contact is significantly shorter than the sum of the van der Waals radii of carbon and sulphur (3.55 Å).[9] Bond lengths and angles of the ligand are not appreciably affected by co-ordination to silver. However, remarkable changes of the ligand conformation are induced. Metal binding at sulphur causes the methionine side chain to unwind completely from the diketopiperazine moiety and the dipeptide ring to assume a buckled conformation, with torsion angles ranging from 0 to 18° and $\beta = 14.7°$. It is possible that the interaction between the S and C(1) atoms stabilizes the planar ring conformation of the uncomplexed ligand and that removal of this interaction by co-ordination at sulphur releases the dipeptide ring to give a buckled conformation.

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