

agitation thermique nettement plus faible que celle observée pour la première forme, en raison, en particulier, d'un plus grand nombre de contacts de van der Waals.

La localisation non ambiguë des atomes d'hydrogène sur le groupe amine confirme les résultats de l'étude de la première forme, notamment ceux obtenus par Plastas & Stewart (1969) qui sont d'une précision comparable à celle de ce travail. La forme 'amino' est donc prépondérante pour les schémas tautomères neutres ou ioniques (Mornon & Raveau, 1971).

Plusieurs molécules de la même série sont en cours de traitement; une discussion et une comparaison

détaillées des résultats seront publiées à l'issue de leur étude.

La liste des facteurs de structure peut être obtenue en s'adressant au Centre de Documentation du C.N.R.S., 26, rue Boyer, Paris 20e, sous le No. A. O. 510.

Références

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
MORNON, J.-P. & RAVEAU, B. (1971). *Acta Cryst.* **B27**, 95.
PLASTAS, L. A. & STEWART, J. M. (1969). *Chem. Commun.* p. 811.

Acta Cryst. (1972). **B28**, 2079

Crystal and Molecular Structure of Ennea-ammonium Dichloride Tetrathiosulphatoargentate, $(\text{NH}_4)_9\text{Cl}_2[\text{Ag}(\text{S}_2\text{O}_3)_4]$

BY F. BIGOLI, A. TIRIPICCHIO AND M. TIRIPICCHIO CAMELLINI

Istituto di Chimica Generale, Università di Parma, Parma, Italy

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The crystal structure of $(\text{NH}_4)_9\text{Cl}_2[\text{Ag}(\text{S}_2\text{O}_3)_4]$ has been determined from X-ray intensity data (Cu $K\alpha$ radiation) measured photographically. The space group is $I\bar{4}2d$ with unit-cell dimensions $a = 13.132$ (8), $c = 16.668$ (10) Å, $V = 2874.4$ Å³, $Z = 4$. The structure was solved by Fourier methods and refined by full-matrix least squares to an R value of 8.4%. The structure consists of $[\text{Ag}(\text{S}_2\text{O}_3)_4]^{7-}$ complexes, and ammonium and chloride ions. The thiosulphato group behaves as a monodentate ligand, bound to silver *via* a sulphur atom. The arrangement of $\text{S}_2\text{O}_3^{2-}$ groups around the silver atom is approximately tetrahedral with bond distances Ag-S = 2.581 Å. The central sulphur of the thiosulphato group is approximately tetrahedral with bond distances S-O = 1.46, 1.47, 1.48 Å and S-S = 2.009 Å. Several hydrogen bonds $\text{N}\cdots\text{O}$ and $\text{N}\cdots\text{Cl}$ hold together the different ions in the crystal structure.

Introduction

Alkaline or ammonium thiosulphates are well known developing agents in photography. The formation of complexes of the thiosulphato group with silver is evidently the main reaction involved in the developing process; however it is not completely certain whether the chlorine atoms take part in the complexes or not. The availability of good crystals of compounds with general formula $\text{M}^1\text{X} \cdot \text{M}^1\text{X} \cdot 4\text{M}_2^1(\text{S}_2\text{O}_3)_4$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ and $\text{M}^1 = \text{NH}_4, \text{K}, \text{M}^1 = \text{Cu}, \text{Ag}$ (Ferrari, Cavalca & Nardelli, 1952), offers the opportunity of giving an answer to this question by determining their crystal structures. The compound $\text{NH}_4\text{Cl} \cdot \text{AgCl} \cdot 4(\text{NH}_4)_2\text{S}_2\text{O}_3$ has been chosen. Possible formulations of this salt are $(\text{NH}_4)_9\text{Cl}_2[\text{Ag}(\text{S}_2\text{O}_3)_4]$ or $2\text{NH}_4\text{Cl} \cdot (\text{NH}_4)_7[\text{Ag}(\text{S}_2\text{O}_3)_4]$.

Experimental

Preparation

Crystals of the compound were obtained by dissolving silver chloride in a saturated solution of ammonium thiosulphate; after one day colourless crystals of the compound separated out. Most of them were well formed bipyramids, pseudo-octahedral.

Crystal data

Compound: $(\text{NH}_4)_9\text{Cl}_2[\text{Ag}(\text{S}_2\text{O}_3)_4]$

Formula weight 789.64

Unit cell parameters (determined from rotation and Weissenberg photographs around [100] and [001],

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å):

$a = 13.132$ (8), $c = 16.668$ (10) Å

$V = 2874.4$ Å³; $Z = 4$

$$D_x = 1.82, D_m = 1.84 \text{ g.cm}^{-3}$$

$$\mu(\text{Cu } K\alpha) = 133.1 \text{ cm}^{-1}; F(000) = 1616$$

Space groups: $I\bar{4}2d$ [$D_{2d}(12)$, No. 122] or $I4_1md$ [$C_{4v}(11)$, No. 109] from systematic absences and the first from structure determination.

Intensity data

In order to avoid effects of discontinuous absorption, a pseudo-octahedral crystal was ground into a cylinder elongated in direction [100] with radius $\bar{R}_{av} = 0.013 \text{ cm}$. Intensities were recorded photographically on an integrating Weissenberg camera and then measured by a microdensitometer. The crystal was rotated around [100] and the reflexions of layers $0kl, \dots, 11kl$ were measured (774 independent reflexions out of a possible 925). Interlayer scaling constants were calculated from common equivalent reflexions.

Calculations

After the usual Lorentz and polarization corrections, the intensities were put on absolute scale by Wilson's (1942) method. Absorption corrections were applied for a cylindrical specimen with $\mu\bar{R} = 1.73$. Atomic scattering factors of Moore (1963) were used; those of Ag, S and Cl were corrected for the real and imaginary part of anomalous dispersion using the values for Af' and Af'' given by *International Tables for X-ray Crystallography* (1965).

The positions of the heavy atoms were determined from a three-dimensional Fourier synthesis obtained

Table 1. Final fractional atomic coordinates ($\times 10^4$) with e.s.d.'s

	x	y	z
Ag	0000	0000	0000
Cl	4907 (7)	2500	1250
S(1)	2491 (2)	-0263 (2)	0979 (2)
S(2)	1469 (2)	0848 (2)	0782 (2)
O(1)	1945 (9)	-1045 (10)	1448 (8)
O(2)	2901 (9)	-0608 (11)	0209 (8)
O(3)	3271 (9)	0213 (9)	1492 (9)
N(1)	0000	0000	5000
N(2)	0000	0000	2456 (33)
N(3)	0532 (16)	7500	1250
N(4)	2757 (13)	3151 (16)	-0056 (14)

Table 2. Thermal parameters (\AA^2) with e.s.d.'s

The B_{ij} values refer to the formula: $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ in which $b_{11} = \frac{1}{4}a^*2B_{11}$, $b_{12} = \frac{1}{2}a^*b^*B_{12}$, etc.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	2.206 (0.037)	2.206 (0.037)	2.513 (0.057)	0	0	0
Cl	3.984 (0.327)	9.281 (0.595)	6.911 (0.397)	0	0	-0.235 (0.427)
S(1)	1.979 (0.100)	2.129 (0.111)	2.293 (0.094)	0.132 (0.084)	-0.433 (0.089)	0.101 (0.080)
S(2)	2.092 (0.116)	3.065 (0.144)	3.860 (0.153)	0.791 (0.009)	-0.611 (0.115)	-0.940 (0.124)
O(1)	2.875 (0.442)	4.212 (0.539)	4.664 (0.566)	-1.683 (0.442)	-1.190 (0.408)	2.187 (0.475)
O(2)	2.237 (0.398)	4.560 (0.538)	3.385 (0.465)	0.883 (0.386)	-0.230 (0.358)	-0.641 (0.423)
O(3)	3.029 (0.422)	2.280 (0.444)	5.100 (0.540)	-0.260 (0.317)	-1.545 (0.410)	-0.680 (0.393)
N(1)	4.456 (0.852)	4.456 (0.852)	5.162 (1.391)	0	0	0
N(2)	11.971 (2.718)	6.983 (1.795)	5.885 (1.411)	-3.299 (2.208)	0	0
N(3)	4.064 (0.784)	2.240 (0.613)	1.002 (0.426)	0	0	0.871 (0.464)
N(4)	3.435 (0.636)	5.809 (0.855)	6.160 (0.882)	-0.387 (0.566)	1.942 (0.720)	-3.124 (0.876)

by putting the silver atom at the origin. The other non-hydrogen atoms were located by further Fourier syntheses. The refinement was carried out by means of cycles of full-matrix least squares, minimizing the function $\sum w|DF|^2$; at the beginning isotropic, and in the later cycles anisotropic, thermal parameters were introduced. Unit weights were used at first, then the scheme $1/w = (A + BF_0)^2$ was assumed; coefficients $A = 3.4$ and $B = 0.0729$ were determined by plotting ΔF against $|F_0|$. In this way R improved to the final value 8.4%.

The final atomic coordinates are quoted in Table 1 and the thermal parameters in Table 2. A list of the observed and calculated structure factors is available as Supplementary Publication No. SUP 30006 (7pp.).*

All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programs written by Immirzi (1967).

Discussion of the structure

An analysis of the distribution of the atomic species over the various possible crystallographic positions shows that the multiplicities of silver and thiosulphato groups are in the ratio 1:4, suggesting that all the thiosulphato groups are bound to one silver atom. The existence of a tetrathiosulphate silver anion then follows (Fig. 1) provided that the chlorine atoms are not in the coordination sphere of the metal. This situation is different from that found in the complex anion $[\text{Cu}_n(\text{S}_2\text{O}_3)_{2n}]^{3n-}$ (Ferrari, Braibanti & Tiripicchio, 1966) where thiosulphato groups bridge different cations, thus forming chains. The thiosulphato group is bound to silver *via* the sulphur atom (Table 3). The arrangement of $\text{S}_2\text{O}_3^{2-}$ groups is approximately tetrahedral, the angles S(2)-Ag-S(2) being 104.8 and 119.3°. The silver-sulphur bonds are Ag-S(2) = 2.581 Å, which can be compared with values in the range 2.48-2.60 Å

* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30006. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Cavalca, Mangia, Palmieri & Pelizzi, 1969) and with the sum of covalent radii 2.56 Å. The central S of the thiosulphato group is approximately tetrahedral with angles $\text{S}(2)\text{--S}(1)\text{--O}(2) = 109.1$, $\text{O}(2)\text{--S}(1)\text{--O}(3) = 112.6$, $\text{O}(1)\text{--S}(1)\text{--O}(3) = 109.0$, $\text{O}(1)\text{--S}(1)\text{--S}(2) = 105.5$, $\text{S}(2)\text{--S}(1)\text{--O}(3) = 104.5^\circ$ and $\text{O}(2)\text{--S}(1)\text{--O}(1) = 115.3^\circ$ and bond distances $\text{S}(1)\text{--S}(2) = 2.009$, $\text{S}(1)\text{--O}(1) = 1.48$, $\text{S}(1)\text{--O}(2) = 1.46$ and $\text{S}(1)\text{--O}(3) = 1.47$ Å. These values agree with those found in thiosulphates (Sándor & Csordás, 1961; Nardelli & Fava, 1962; Nardelli, Fava & Giraldi, 1962; Ferrari, Braibanti & Tiripicchio, 1966; Andreotti, Cavalca, Domiano & Musatti, 1968; Baggio, Amzel & Becka, 1969; Fava Gasparri, Mangia, Musatti & Nardelli, 1969; Padmanabhan, Yadava, Navarro, Garcia, Karsono, Suh & Chien, 1971) although the S–S distance 2.009 Å is shorter than that expected according

to Baggio, Amzel & Becka (1970) in a monodentate thiosulphato ligand.

The distribution of ammonium ions in different crystallographic positions (Fig. 2) raises the question whether all of them have the same chemical function,

Table 3. Bond distances and angles in the complex $[\text{Ag}(\text{S}_2\text{O}_3)_4]^{7-}$

Ag–S(2)	2.581 (3) Å	S(2)–Ag–S(2 ⁱ)	104.8 (1)°
		S(2)–Ag–S(2 ⁱⁱ)	119.3 (1)
S(1)–S(2)	2.009 (4)	O(1)–S(1)–S(2)	105.5 (5)
S(1)–O(1)	1.48 (1)	S(2)–S(1)–O(3)	104.5 (5)
S(1)–O(2)	1.46 (1)	O(3)–S(1)–O(2)	112.6 (7)
S(1)–O(3)	1.47 (1)	O(2)–S(1)–O(1)	115.3 (8)
		O(1)–S(1)–O(3)	109.0 (8)
		O(2)–S(1)–S(2)	109.1 (6)

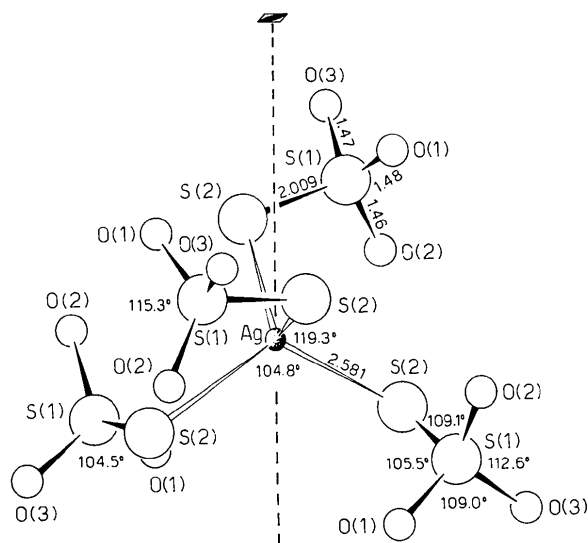


Fig. 1. Bond distances and angles in the complex $[\text{Ag}(\text{S}_2\text{O}_3)_4]^{7-}$

Table 4. Hydrogen bonds

Cl \cdots N(4 ⁱⁱⁱ)	3.25 (2) Å	N(4 ⁱⁱⁱ)–Cl–N(4 ⁱⁱⁱ)	76.7 (6)°
Cl \cdots N(4 ^{iv})	3.25 (2)		
N(1) \cdots O(3 ^v)	2.84 (1)	O(3 ^v)–N(1)–O(3 ^{vi})	110.5 (4)
N(1) \cdots O(3 ^{vi})	2.84 (1)	O(3 ^v)–N(1)–O(3 ^{viii})	107.4 (4)
N(1) \cdots O(3 ^{vii})	2.84 (1)		
N(1) \cdots O(3 ^{viii})	2.84 (1)		
N(2) \cdots O(2 ^v)	2.90 (2)	S(2)–N(2)–S(2 ⁱ)	77.2 (11)
N(2) \cdots O(2 ^{viii})	2.90 (2)	S(2)–N(2)–O(2 ^v)	70.6 (6)
N(2) \cdots S(2 ⁱ)	3.57 (4)	O(2 ^v)–N(2)–O(2 ^{viii})	163.3 (2.2)
N(2) \cdots S(2)	3.57 (4)		
N(3) \cdots O(1 ^{ix})	2.68 (2)	O(1 ^{ix})–N(3)–O(2 ^{xii})	97.1 (4)
N(3) \cdots O(1 ^x)	2.68 (2)	O(1 ^{ix})–N(3)–O(1 ^x)	92.5 (8)
N(3) \cdots O(2 ^{xi})	2.90 (2)	O(1 ^{ix})–N(3)–O(2 ^{xii})	126.1 (4)
N(3) \cdots O(2 ^{xii})	2.90 (2)	O(2 ^{xi})–N(3)–O(2 ^{xii})	117.9 (8)
N(4)–O(1 ^{xiii})	2.78 (2)	O(2 ⁱⁱ)–N(4)–O(3 ^x)	112.0 (8)
N(4)–O(2 ⁱⁱ)	2.85 (2)	O(2 ⁱⁱ)–N(4)–O(1 ^{xiii})	116.1 (8)
N(4)–O(3 ^x)	2.87 (3)	O(2 ⁱⁱ)–N(4)–Cl(^{xii})	86.2 (6)
N(4)–Cl(^{xii})	3.25 (2)	O(3 ^x)–N(4)–O(1 ^{xiii})	131.5 (7)
		O(3 ^x)–N(4)–Cl(^{xii})	77.8 (5)
		O(1 ^{xiii})–N(4)–Cl(^{xii})	98.0 (7)

Table 4 (cont.)

Asymmetric units:

i	$-x, -y, z$	vii	$x - \frac{1}{2}, -y, \frac{3}{4} - z$
ii	$-y, x, -z$	viii	$y, x - \frac{1}{2}, \frac{1}{4} + z$
iii	$1 - y, x, -z$	ix	$x, y + 1, z$
iv	$1 - y, \frac{1}{2} - x, \frac{1}{4} + z$	x	$x, \frac{1}{2} - y, \frac{1}{4} - z$
v	$-y, \frac{1}{2} - x, \frac{1}{4} + z$	xi	$y, \frac{1}{2} + x, \frac{1}{4} + z$
vi	$\frac{1}{2} - x, y, \frac{3}{4} - z$	xii	$y, 1 - x, -z$
		xiii	$\frac{1}{2} + y, x, -\frac{1}{4} + z$

in other words whether the crystal is composed of two distinct salts NH_4Cl and $(\text{NH}_4)_7\text{Ag}(\text{S}_2\text{O}_3)_4$ or whether NH_4^+ and Cl^- ions are distributed in the crystal structure in order to fill the voids and balance the charges. From an analysis of the features of this crystal structure it is apparent that species N(1), N(3), N(4) play the role of joining the complex anions $\text{Ag}(\text{S}_2\text{O}_3)_4^{7-}$ to one another whereas N(2) and Cl are not essential

for the stability of the structure itself. Although such statement could be proved only by preparing crystals without NH_4Cl molecules, it seems to give a general picture of the compound on study, which could therefore be formulated as $(\text{NH}_4)_7[\text{Ag}(\text{S}_2\text{O}_3)_4] \cdot 2\text{NH}_4\text{Cl}$.

The environments of the nitrogen and chlorine atoms are reported in Table 4. N(1) forms four hydrogen bonds $\text{NH} \cdots \text{O}(3) = 2.84 \text{ \AA}$ with four different complexes $\text{Ag}(\text{S}_2\text{O}_3)_4^{7-}$. N(3) is shared by two different complexes $\text{Ag}(\text{S}_2\text{O}_3)_4^{7-}$ via two strong hydrogen bonds $\text{N}(3) \cdots \text{O}(1) = 2.68 \text{ \AA}$ and two weaker ones $\text{N}(3) \cdots \text{O}(2) = 2.90 \text{ \AA}$. N(4) bridges three such complexes via rather strong hydrogen bonds $\text{N}(4) \cdots \text{O}(1) = 2.78$, $\text{N}(4) \cdots \text{O}(2) = 2.85$ and $\text{N}(4) \cdots \text{O}(3) = 2.87 \text{ \AA}$. The fourth position around N(4) is occupied by Cl which also forms a hydrogen bond $\text{N}(4) \cdots \text{Cl} = 3.25 \text{ \AA}$. The atom N(2) is less tightly bound; it forms two hydrogen

bonds $\text{N}(2) \cdots \text{O}(2) = 2.90 \text{ \AA}$ with different complexes; two further contacts with sulphur atoms $\text{N}(2) \cdots \text{S}(2) = 3.57 \text{ \AA}$ complete the coordination sphere of N(2).

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References

- ANDRETTI, G. D., CAVALCA, L., DOMIANO, P. & MUSATTI, A. (1968). *Ric. Sci.* **38**, 1100.
 BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 2650.
 BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1970). *Acta Cryst.* **B26**, 1698.
 CAVALCA, L., MANGIA, A., PALMIERI, C. & PELIZZI, G. (1969). *Inorg. Chim. Acta*, **4**, 299.

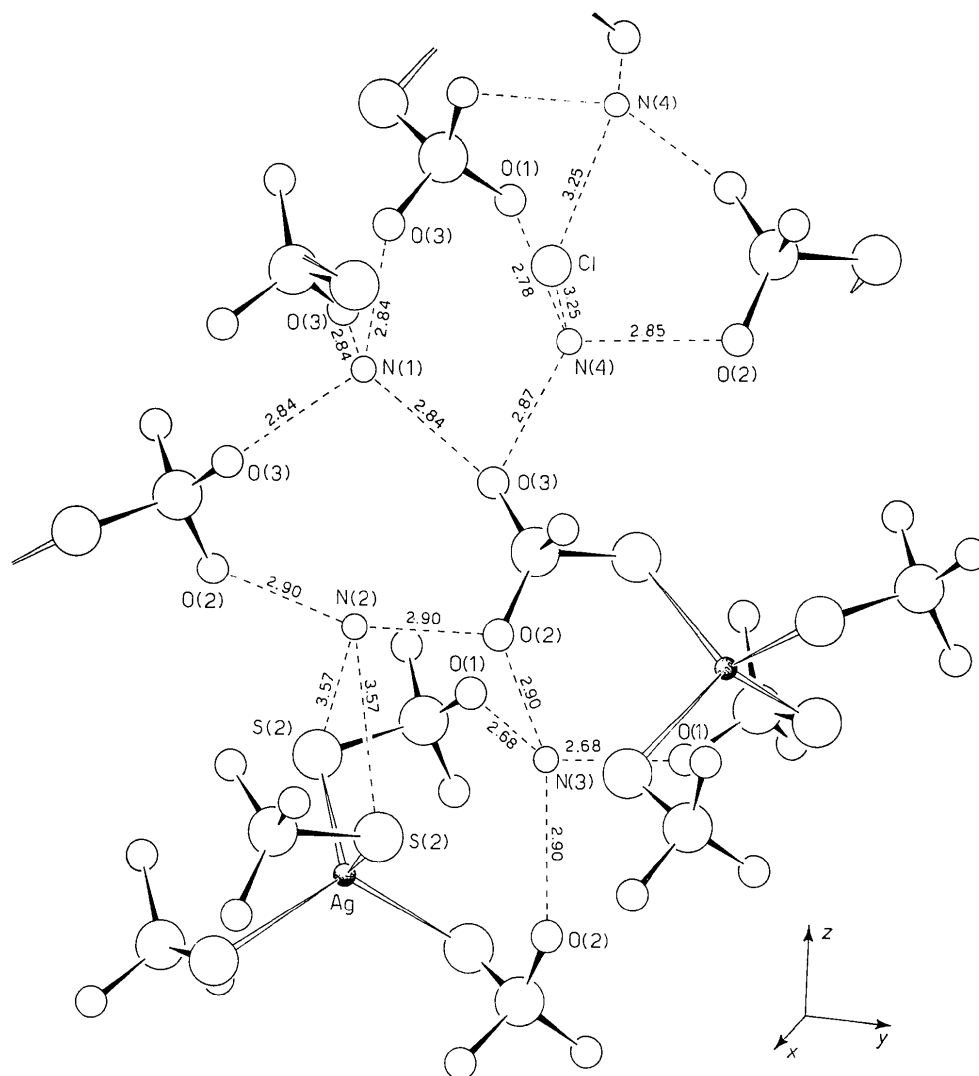


Fig. 2. Clinographic projection of the structure.

- FAVA GASPARRI, G., MANGIA, A., MUSATTI, A. & NARDELLI, M. (1969). *Acta Cryst.* B25, 203.
- FERRARI, A., CAVALCA, L. & NARDELLI, M. (1952). *Gazz. Chim. Ital.* 82, 406.
- FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1966). *Acta Cryst.* 21, 605.
- IMMIRZI, A. (1967). *Ric. Sci.* 37, 743.
- International Tables for X-ray Crystallography* (1965). Vol. III. Birmingham: Kynoch Press.
- MOORE, F. H. (1963). *Acta Cryst.* 16, 1169.
- NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* 15, 227.
- NARDELLI, M. & FAVA, G. (1962). *Acta Cryst.* 15, 477.
- PADMANABHAN, V. M., YADAVA, V. S., NAVARRO, Q. O., GARCIA, A., KARSONO, L., SUH, H. & CHIEN, L. S. (1971). *Acta Cryst.* B27, 253.
- SÁNDOR, E. & CSORDÁS, L. (1961). *Acta Cryst.* 14, 237.
- WILSON, A. J. C. (1942). *Nature, Lond.* 150, 152.

Acta Cryst. (1972). B28, 2083

Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. II.* The Crystal and Molecular Structure of the Dipeptide Glycylglycine Monohydrochloride Monohydrate†

BY THOMAS F. KOETZLE,‡ WALTER C. HAMILTON,

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

AND R. PARTHASARATHY

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14203, U.S.A.

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Glycylglycine monohydrochloride monohydrate, $C_4N_2O_3H_9Cl \cdot H_2O$, crystallizes in the monoclinic system with $a=8.813$ (3), $b=9.755$ (3), $c=9.788$ (3) Å and $\beta=104.10$ (2)°, space group $P2_1/c$ and $Z=4$. The crystal structure has been refined by neutron diffraction, and all hydrogen atoms have been located precisely. Average bond distances to hydrogen within the dipeptide molecule are: C–H 1.086, N–H 1.028 and O–H 1.003 Å (all ± 0.006 Å). All features involving heavy atoms are nearly identical with those found in the structure determined by X-ray diffraction. The neutron diffraction results indicate the presence of a network of seven distinct hydrogen bonds in the crystal. Three other short N–H...O and N–H...Cl contacts in the crystal structure should probably not be considered as being hydrogen bonds.

Introduction

Interactions involving hydrogen atoms play a large role in determining the configurations of polypeptides and proteins. Detailed information about hydrogen atom stereochemistry in amino acids and small peptides may provide important insights into the action of intramolecular forces in larger systems. A neutron diffraction study of glycylglycine hydrochloride was undertaken in order to determine accurately the positions of hydrogen atoms in this simple dipeptide and to allow a complete examination of hydrogen bonding in the crystal.

Crystal data

Glycylglycine monohydrochloride monohydrate crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$.

The earlier X-ray study (Parthasarathy, 1969) established the cell dimensions: $a=8.813$ (3), $b=9.755$ (5), $c=9.788$ (3) Å, and $\beta=104.10$ (2)°. The density calculated from this unit cell is 1.513 g.cm^{-3} .

Experimental

Large single crystals grown by slow evaporation from aqueous solution were elongated in the direction of the c axis with major faces $\{110\}$. A well-formed sample whose bounding planes are given in Table I was mounted on a four-circle neutron diffractometer at the Brookhaven High Flux Beam Reactor. The c^* axis of the crystal was aligned approximately along the diffractometer ϕ axis. Data were collected automatically using the Brookhaven Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966) with a crystal-monochromatized neutron beam of wavelength 1.038 Å. The increment between points in the θ - 2θ step scan was 0.12°. Data for 3170 reflections having values of $(\sin \theta)/\lambda$ between 0.1 and 0.7 were reduced to integrated intensities and corrected for absorption using programs from the Brookhaven CDC 6600 Crystallographic Computing Library.

* Part III has already been published (Jönsson & Kvik, *Acta Cryst.* (1972), B28, 1827).

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‡ U.S. National Institutes of Health Postdoctoral Fellow.