

Each Ni atom is coordinated in an essentially octahedral geometry by four oxime N atoms of two oaoH<sub>2</sub> molecules, and two carboxyl O atoms of different (but crystallographically equivalent) mellitic acid anions. These O atoms occupy *cis* positions, as is always found in octahedral  $[\text{NiX}_2(\text{oaoH}_2)_2]$  complexes (Endres, 1984; Endres & Schendzielorz, 1983b).

Each mellitic acid anion bridges four Ni centers. This results in a one-dimensional ribbon-like structure extending parallel to *a* (Fig. 2). Empty space left by this arrangement is filled with water molecules.

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## Structure of Bis(9-methylhypoxanthine)silver(I) Nitrate Dihydrate, $[\text{Ag}(\text{C}_6\text{H}_6\text{N}_4\text{O})_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$

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**Abstract.**  $M_r = 506.2$ , triclinic,  $P\bar{1}$ ,  $a = 9.985$  (3),  $b = 14.655$  (4),  $c = 6.606$  (2) Å,  $\alpha = 107.26$  (3),  $\beta = 95.92$  (3),  $\gamma = 96.71$  (3)°,  $V = 907.0$  (7) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.84$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54182$  Å,  $\mu(\text{Cu } K\alpha) = 10.01$  mm<sup>-1</sup>,  $F(000) = 508$ , room temperature,  $R = 0.066$  for 2532 observed reflections. The Ag<sup>+</sup> ion is linearly bonded to the two 9-methylhypoxanthine ligands through the N(7) sites. The structure of the metal-bridged base–base pair is in the *syn* configuration with respect to the N(7)–Ag–N(7) bond and stabilized by a water bridge between the carbonyl O atoms O(6).

**Introduction.** Shin & Eichhorn (1980) have shown that the Ag<sup>+</sup> ion reacts with polyinosinic acid to form a 1:2 complex at low pH, with no proton release, and they have proposed a double-helix structure with N(7)–Ag<sup>+</sup>–N(7) bonding. Structurally, two arrangements with N(7)–metal–N(7) bonding are possible, as shown in Fig. 1. Of the (I) *syn* and (II) *anti* configurations, the type (I) structure has, in fact, been exemplified in the crystal structure of  $[\text{Ag}(9\text{-methylhypoxanthine})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$  (Gariépy &

Beauchamp, 1980). We have determined the crystal structure of the nitrate salt of Ag<sup>+</sup>–9-methylhypoxanthine in the hope of finding the type (II) structure.

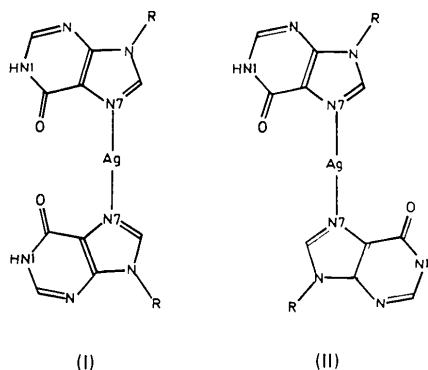


Fig. 1. A schematic representation of the two possible structures with N(7)–Ag–N(7) bonding for the 1:2 Ag–polyinosinic acid system: (I) *syn* and (II) *anti* configurations of the ligands with respect to N–Ag–N.

Table 1. Positional parameters ( $\times 10^4$ , for Ag  $\times 10^5$ ) and equivalent isotropic temperature factors ( $B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$ ) with e.s.d.'s in parentheses for non-H atoms

	x	y	z	$B_{eq}(\text{\AA}^2)$
Ag	41622 (8)	21119 (5)	44323 (12)	4.22 (0.02)
N(11)	6644 (7)	5578 (5)	8264 (11)	4.0 (0.2)
C(12)	5826 (9)	6269 (6)	8805 (13)	3.9 (0.3)
N(13)	4509 (7)	6126 (5)	8489 (11)	4.0 (0.2)
C(14)	4012 (9)	5163 (6)	7549 (13)	3.6 (0.3)
C(15)	4743 (9)	4424 (6)	6935 (12)	3.5 (0.2)
C(16)	6178 (9)	4582 (6)	7271 (14)	3.9 (0.3)
O(16)	6976 (7)	4017 (5)	6834 (11)	5.3 (0.2)
N(17)	3803 (7)	3552 (5)	6000 (11)	4.0 (0.2)
C(18)	2593 (9)	3807 (6)	6081 (14)	4.1 (0.3)
N(19)	2651 (7)	4785 (5)	7025 (11)	3.8 (0.2)
C(19)	1528 (10)	5316 (8)	7459 (17)	5.3 (0.3)
N(21)	7787 (7)	52 (5)	2935 (12)	4.4 (0.2)
C(22)	7416 (9)	-936 (7)	2215 (15)	4.6 (0.3)
N(23)	6157 (7)	-1375 (5)	1712 (12)	4.3 (0.2)
C(24)	5238 (8)	-752 (6)	2011 (12)	3.3 (0.2)
C(25)	5520 (8)	256 (6)	2765 (13)	3.4 (0.2)
C(26)	6882 (10)	708 (6)	3329 (14)	4.3 (0.3)
O(26)	7274 (7)	1595 (5)	3998 (12)	5.8 (0.2)
N(27)	4344 (8)	626 (5)	2867 (11)	4.1 (0.2)
C(28)	3316 (9)	-140 (6)	2168 (14)	4.2 (0.3)
N(29)	3857 (7)	-982 (5)	1625 (11)	3.7 (0.2)
C(29)	3062 (10)	-1969 (6)	834 (16)	4.9 (0.3)
O(W1)	9308 (7)	3153 (5)	6307 (13)	6.2 (0.3)
O(W2)	764 (8)	3372 (6)	283 (14)	7.2 (0.3)
N(1)	627 (8)	1362 (6)	2200 (14)	5.3 (0.3)
O(1)	1621 (8)	1959 (6)	2251 (14)	7.8 (0.3)
O(2)	-299 (9)	1176 (8)	674 (16)	9.4 (0.4)
O(3)	585 (8)	930 (6)	3539 (13)	6.9 (0.3)

**Experimental.** Colourless needles, elongated along **c**, slightly photosensitive, obtained from an aqueous solution (pH *ca* 5) containing 9-methylhypoxanthine and  $\text{AgNO}_3$  ( $10^{-4}$  mol, 1:1 ratio).  $D_m$  not measured. Crystal  $0.10 \times 0.15 \times 0.60$  mm. Stoe four-circle diffractometer, Ni-filtered  $\text{Cu K}\alpha$  radiation. Cell parameters refined by least squares with 15 independent  $2\theta$  values.  $2\theta \leq 120^\circ$  ( $\pm h \pm k \pm l$  set),  $\theta$ - $2\theta$  scan mode. 2885 reflections measured, 2532 with  $F_o > 3\sigma(F_o)$  used for the structure determination. Three reference reflections: no systematic intensity variation. Absorption correction using an axial reflection (at  $\chi \sim -90^\circ$ ), transmission coefficients 0.71 to 1.10 (normalized to an average of unity). Structure solved by Patterson and Fourier methods. Block-diagonal least-squares refinement with anisotropic thermal parameters for non-H atoms, H atoms (from a difference map) isotropic;  $\sum w(F_o - |F_c|)^2$  minimized;  $w = 1.0$  for  $F_o \leq 50.0$  and  $\sqrt{w} = 50.0/F_o$  for  $F_o > 50.0$ ; final  $R = 0.066$  and  $R_w = 0.072$  for 2532 observed reflections. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).  $(\Delta/\sigma)_{\text{max}} = 0.18$ . Max. peak in final  $\Delta\rho$  map  $1.7 \text{ e \AA}^{-3}$  near Ag atom. Calculations carried out on a FACOM M380 computer at the Institute of Physical and Chemical Research with the UNICSIII program system (Sakurai & Kobayashi, 1979).

Table 2. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with estimated standard deviations in parentheses

(1) The coordination sphere			
Ag-N(17)	2.147 (7)	Ag...O(1)	2.736 (8)
Ag-N(27)	2.154 (7)		
Ag-N(17)-C(15)	130.0 (6)	N(17)-Ag-N(27)	175.1 (3)
Ag-N(17)-C(18)	124.2 (5)	N(17)-Ag...O(1)	82.7 (3)
Ag-N(27)-C(25)	125.6 (5)	N(27)-Ag...O(1)	93.6 (3)
Ag-N(27)-C(18)	126.8 (6)		
(2) The 9-methylhypoxanthine ligands			
	Ligand (1)	Ligand (2)	
N(1)-C(2)	1.363 (12)	1.374 (12)	
C(2)-N(3)	1.293 (12)	1.305 (11)	
N(3)-C(4)	1.369 (10)	1.357 (12)	
C(4)-C(5)	1.363 (12)	1.394 (11)	
C(5)-C(6)	1.408 (13)	1.402 (12)	
C(6)-N(1)	1.410 (10)	1.383 (13)	
C(6)-O(6)	1.210 (12)	1.242 (11)	
C(5)-N(7)	1.425 (10)	1.350 (12)	
N(7)-C(8)	1.307 (12)	1.362 (11)	
C(8)-N(9)	1.374 (11)	1.369 (12)	
N(9)-C(4)	1.373 (10)	1.359 (10)	
N(9)-C(9)	1.444 (13)	1.482 (11)	
N(1)-C(2)-N(3)	126.1 (7)	124.2 (9)	
C(2)-N(3)-C(4)	110.8 (7)	112.8 (8)	
N(3)-C(4)-C(5)	127.4 (8)	126.9 (7)	
C(4)-C(5)-C(6)	121.7 (7)	119.1 (8)	
C(5)-C(6)-N(1)	108.9 (8)	112.3 (7)	
C(6)-N(1)-C(2)	125.0 (7)	124.6 (8)	
N(1)-C(6)-O(6)	120.8 (8)	121.9 (9)	
C(5)-C(6)-O(6)	130.3 (8)	125.7 (9)	
C(4)-C(5)-N(7)	107.8 (7)	109.8 (7)	
C(5)-N(7)-C(8)	105.6 (7)	106.6 (7)	
N(7)-C(8)-N(9)	112.5 (7)	109.4 (8)	
C(8)-N(9)-C(4)	105.9 (7)	108.2 (7)	
N(9)-C(4)-C(5)	108.2 (7)	106.1 (7)	
N(9)-C(4)-N(3)	124.4 (8)	127.0 (7)	
C(6)-C(5)-N(7)	130.4 (8)	131.1 (8)	
C(4)-N(9)-C(5)	126.2 (7)	126.4 (7)	
C(8)-N(9)-C(9)	127.9 (7)	125.4 (7)	
(3) The nitrate anion			
N(1)-O(1)	1.235 (12)	N(1)-O(3)	1.232 (14)
N(1)-O(2)	1.238 (12)		
O(1)-N(1)-O(2)	116.9 (11)	O(2)-N(1)-O(3)	121.2 (9)
O(1)-N(1)-O(3)	121.8 (9)		

Table 3. Hydrogen bonds

Donor (D)	Acceptor (A)	$D \cdots A$ ( $\text{\AA}$ )
N(11)	O(W2)	2.769 (10)
N(21)	O(3 <sup>ii</sup> )	2.871 (10)
O(W1)	O(16)	2.782 (10)
O(W1)	O(26)	2.806 (8)
O(W2)	O(1)	2.915 (14)
O(W2)	O(W1 <sup>iii</sup> )	2.778 (12)
C(18)	O(1)	3.081 (11)
C(28)*	O(3)	3.373 (13)
C(28)*	O(2 <sup>iv</sup> )	3.313 (12)

Symmetry code: none  $x, y, z$ ; (i)  $1-x, 1-y, 1-z$ ; (ii)  $1+x, y, z$ ; (iii)  $x-1, y, z-1$ ; (iv)  $-x, -y, -z$ ; (v)  $1-x, -y, -z$ .

\* C(28) forms bifurcated H bonds with O(3) and O(2<sup>iv</sup>).

**Discussion.** Final atomic parameters are in Table 1.\* Selected bond distances and angles are listed in Table 2. Hydrogen-bonding contacts are in Table 3.

A perspective view of the complex is shown in Fig. 2. The  $\text{Ag}^+$  ion is linearly attached to the two independent 9-methylhypoxanthine ligands through the ring N(7) sites. The  $\text{Ag}-\text{N}$  bond lengths [2.147 (7) and 2.154 (7) Å] are in the normal range observed for other nucleic acid bases: 1-methylthymine, 2.181 (4) Å (Guay & Beauchamp, 1979); 1-methyluracil, 2.08 (3) Å (Aoki & Saenger, 1984); 9-methylhypoxanthine, 2.13 (1)<sub>av</sub> Å (Gariépy & Beauchamp, 1980); 9-methyladenine, 2.154 (9)–2.183 (9) Å (Gagnon & Beauchamp, 1977); adenine, 2.16 (1) and 2.20 (1) Å (Gagnon, Hubert, Rivest & Beauchamp, 1977); and 1-methylcytosine, 2.225 (2) Å (Kistenmacher, Rossi & Marzilli, 1979). Though the  $\text{Ag}^+$  ion is basically two-coordinated, it also makes a close contact with nitrate oxygen O(1) (indicated by double broken lines in Fig. 2); the  $\text{Ag}\cdots\text{O}$  distance of 2.736 (8) Å may be too long to be considered a true coordinative bond but suggests significant, probably ionic, interactions between them. The hypoxanthine ligands are arranged in a *syn* configuration with respect to the N(7)– $\text{Ag}$ –N(7) bond and they are nearly

\* Lists of structure factors, positional parameters with isotropic temperature factors for H atoms, anisotropic temperature factors for non-H atoms, bond lengths and angles involving H atoms, the least-squares planes of the purine rings, and hydrogen-bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39181 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

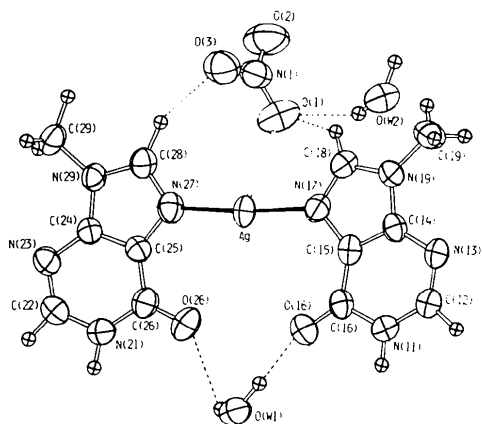


Fig. 2. The asymmetric unit of  $[\text{Ag}(9\text{-methylhypoxanthine})_2]\cdot(\text{NO}_3)\cdot 2\text{H}_2\text{O}$ , showing the linear  $\text{Ag}^+$  bonding to two ligand N(7) atoms and the *syn* structure. Covalent and coordinative bonds are respectively drawn as open and solid (also in Fig. 3). Double broken lines indicate an ionic interaction between  $\text{Ag}^+$  and a nitrate anion O(1), and single broken lines show H bonds. Note a water bridge between two carbonyl O(6) atoms. The thermal ellipsoids are drawn at the 50% probability level except for H atoms which are artificially set at  $B = 1.0 \text{ \AA}^2$ .

coplanar. This structural geometry seems to be significantly stabilized by a water bridge *via* hydrogen bonds to the carbonyl O(6) [O(16) $\cdots$ O(W1) $\cdots$ O(26) 2.782 (10) and 2.806 (8) Å]. Molecular dimensions in the 9-methylhypoxanthine ligands are similar to each other, to those found in the metal-free ligand (Kim & Rich, 1967), and to those in the N(7)–metal-bonded hypoxanthine nucleotides (Aoki, 1975; Sletten, 1974; Sletten & Kaale, 1977).

As shown in Fig. 3, the crystal packing is dominated by extensive stacking interactions between the bases [ligand (1) $\cdots$ ligand (1) = 3.261 (6) and 3.289 (6) Å, and ligand (2) $\cdots$ ligand (2) = 3.28 (1) and 3.32 (1) Å, average spacings] and by hydrogen-bonding interactions involving nitrate and water of crystallization molecules (see also Table 3). Nucleotide–anion interactions are important in connection with the denaturation power of anions on nucleic acids (Hamaguchi & Geiduschek, 1962; Sletten & Fløgstad, 1976). A nitrate anion in the complex interacts with the hypoxanthine bases in two manners: one is as an intramolecular bridge between the ligands (1) and (2) through hydrogen bonds, C(18)–H $\cdots$ O(1)–N(1)–O(3) $\cdots$ H–C(28) (Fig. 2), and the other as an intermolecular one between ligands (2) which are stacked on each other, N(21)–H $\cdots$ O(3<sup>ii</sup>)–N(1<sup>ii</sup>)–O(2<sup>ii</sup>) $\cdots$ H–C(28<sup>v</sup>) (Fig. 3 and Table 3).

The molecular structure of the present complex is essentially equivalent to that of the corresponding perchlorate salt (Gariépy & Beauchamp, 1980). Therefore, the repeated occurrence of the *syn* structure

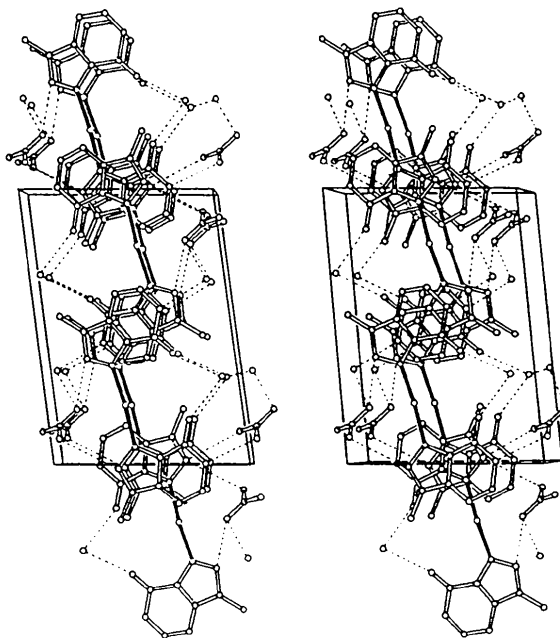


Fig. 3. A stereoview of the crystal packing viewed down the *c* axis, with the *a* axis horizontal, and the *b* axis vertical. Broken lines denote H bonds.

(type I in Fig. 1) stabilized by a water bridge shows the importance of such a water molecule in keeping the structure in the specific configuration. Consequently, though the present analysis has failed to present the *anti* structure (type II in Fig. 1), its possibility cannot be ruled out in different hydration environments around Ag–polyinosinic acid polymers. Furthermore, nucleic acid structures are themselves constrained and their sugar–phosphate backbones are additional factors affecting structures of nucleic acids by interacting with water molecules and/or various ions.

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## Structure of (1-Methyluracilato)silver(I), [Ag(C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub>)]

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(Received 27 October 1983; accepted 31 January 1984)

**Abstract.**  $M_r = 233.0$ , monoclinic,  $C2/c$ ,  $a = 12.537$  (9),  $b = 10.278$  (8),  $c = 9.918$  (6) Å,  $\beta = 104.84$  (5)°,  $V = 1223$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 2.53$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71068$  Å,  $\mu(\text{Mo } K\alpha) = 3.48$  mm<sup>-1</sup>,  $F(000) = 896$ , room temperature,  $R = 0.099$  for 479 observed reflections. The complex is a one-dimensional polymer in which one of the two independent Ag<sup>+</sup> ions is linearly bonded to the two 1-methyluracilate ligands through the deprotonated N(3) sites and another Ag<sup>+</sup> ion tetrahedrally to the four ligands through the two O(2) and two O(4) sites; an N(3)–metal–bonded base–base pair, which involves an inversion center at the metal site, is arranged in *anti* configuration with respect to the N–Ag–N bond and is further cross-linked by two additional metal ions with the formation of eight-membered chelate rings,  $\overline{\text{Ag}(\text{I})-\text{N}(3)-\text{C}(2)-\text{O}(2)-\text{Ag}(2^{\text{I})}-\text{O}(4^{\text{I})}-\text{C}(4^{\text{I})}-\text{N}(3^{\text{I}})}$ .

**Introduction.** Recently, Shin & Eichhorn (1980) have reported that Ag<sup>+</sup> ions react with polyuridylic acid to form

a 1:1 complex at low pH, with one proton released, and they have proposed a double-helical structure with N(3)–Ag–O bonding. In order to aid in the prediction of the structure that might be expected for the Ag–polyuridylic acid system, we have determined the crystal structure of the 1:1 Ag–1-methyluracilate complex. The analogous complex (1-methyl-thyminato)Ag<sup>I</sup> has been reported (Guay & Beauchamp, 1979).

**Experimental.** Colourless needles, elongated along *c*, slightly photosensitive, obtained from an aqueous solution (pH *ca* 5) containing 1-methyluracil and AgNO<sub>3</sub> (10<sup>-4</sup> mol, 1:1 ratio). Crystal 0.02 × 0.03 × 0.15 mm. Rigaku automated four-circle diffractometer, graphite-monochromated Mo *K*α radiation. Cell parameters refined by least squares with 13 independent  $2\theta$  values.  $2\theta \leq 45^\circ$  ( $\pm h \pm k + l$  set),  $\omega$ – $2\theta$  scan mode. 956 reflections measured, 479 with  $F_o > 3\sigma(F_o)$  used for the structure determination. Three reference