catena-Poly[[*μ*-ethylenediamine-*κ²N:N′*-bis[(ethylenediamine-*κ²N,N′*)silver(I)]bis[silver(I)-*μ*-barbiturato-*κ²N:N′*]] dihydrate]

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The title compound, $\{[Ag_2(C_2H_8N_2)_3][Ag_2(C_8H_{10}N_2O_3)_2]\cdot 2H_2O\}_n$, consists of one-dimensional polymeric silver(I) complex anionic chains, discrete dinuclear silver(I) complex cations and solvent water molecules. In the anionic chain, each Ag^I atom is coordinated by two deprotonated N atoms from two barbiturate ligands in a perfectly linear geometry. In the dinuclear silver(I) complex cation, each Ag^I atom, in a Y-shaped coordination environment, is coordinated by three N atoms from two ethylenediamine molecules. The bridging ethylenediamine ligand and the Ag atoms of the anionic chain lie on inversion centres.

Comment

Over the years, there has been a continuous interest in the chemistry of metal complexes of biologically important ligands. The study of such complexes may lead to a greater understanding of the role of the ligand in biological systems and may also contribute to the development of new metal-based chemotherapeutic agents. The barbituric acids are one such class of biologically active compounds, the coordination chemistry of which has been investigated, since such metal complexes are important in the detection and identification of the barbiturate drugs. Barbituric acids coordinate through one or both deprotonated N atoms and ketone O atoms. Most studies have concentrated on the first-row transition metals (Caira *et al.*, 1973; Nassimbeni & Rodgers, 1974; Cotton *et al.*, 1991) and relatively few studies have concerned barbituric acid complexes of platinum-group metals (Sinn *et al.*, 1978; Fawcett *et al.*, 1996) or silver and gold (Bonati *et al.*, 1986). We report here the crystal structure of a novel silver(I) complex with barbiturate and ethylenediamine ligands.

(I)
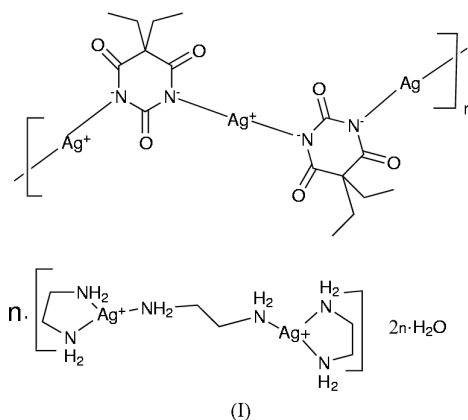
The title compound, (I), consists of a one-dimensional polymeric silver(I) complex anionic chain, $[Ag_2(C_8H_{10}N_2O_3)_2]_n^{2n-}$, discrete dinuclear silver(I) complex
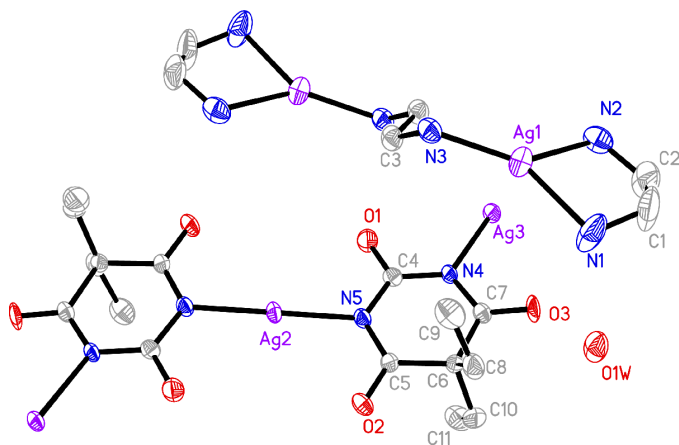
Figure 1
The asymmetric unit of (I), together with the other half of the cation and a second segment of the polymeric anion,, showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity.
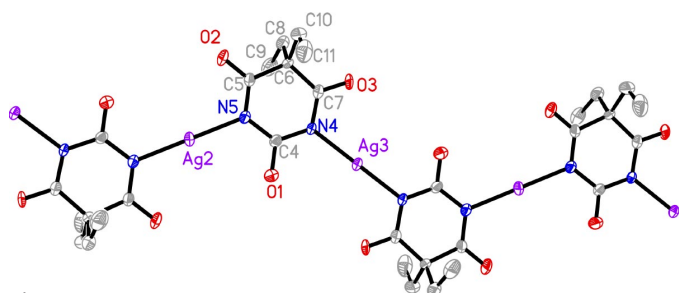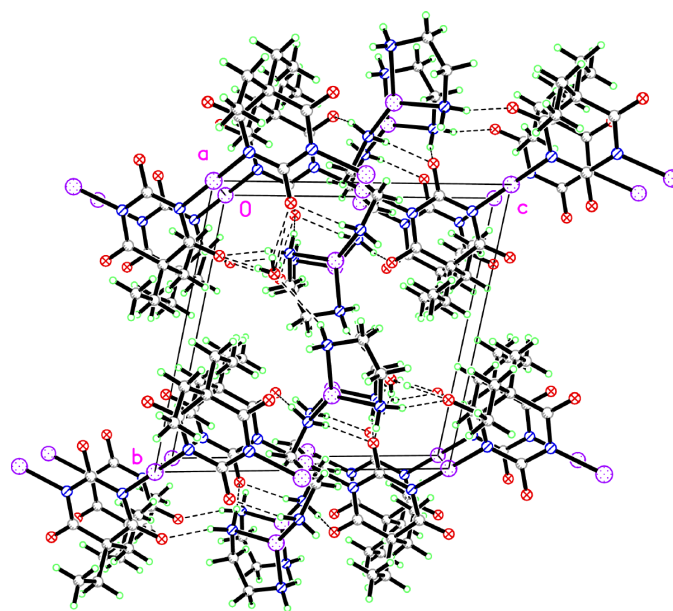

Figure 2
Part of the $[Ag_2(C_8H_{10}N_2O_3)_2]_n^{2n-}$ chain, showing the coordination of Ag^I atoms with barbiturate ligands. H atoms have been omitted for clarity.

cations, $n[(Ag_2(C_2H_8N_2)_3]^{2+}$, and $2nH_2O$ molecules. The asymmetric unit of (I) is shown in Fig. 1. In the anionic chain (Fig. 2), each Ag^I atom is coordinated by two deprotonated N atoms from two barbiturate ligands [Ag2—N5 = 2.125 (6) Å and Ag3—N4 = 2.118 (6) Å]. The Ag^I atoms of the anionic chain lie on inversion centres and show a perfectly linear geometry. In the centrosymmetric dinuclear silver(I) complex cation, each Ag^I atom is three-coordinated by two N atoms from one ethylenediamine molecule and one N atom from an ethylenediamine molecule which acts as a bridge between the two Ag atoms. The Ag—N distances range from 2.183 (7) to 2.339 (8) Å, which are longer than those observed in similar ethylenediamine–silver(I) complexes [2.123 (5)–2.166 (5) Å; Chen *et al.*, 2003; Zhu, Sun *et al.*, 2003; Zhu, Wang, Meng & Liu, 2003; Zhu, Zhang *et al.*, 2003; Zhu, Wang, Sun & Wang, 2003]. The N—Ag—N bond angles (Table 1) indicate a Y-shaped coordination environment of atom Ag1.

N—H⋯O and O—H⋯O hydrogen bonds (Table 2) link the ionic complexes and water molecules into a three-dimensional network (Fig. 2).

Experimental

Ag2O (0.5 mmol, 116 mg) and barbituric acid (1 mmol, 184 mg) were dissolved in a solution of acetonitrile and concentrated aqueous

Figure 3
The crystal packing of (I), viewed down the *a* axis. O—H⋯O and N—H⋯O hydrogen bonds are shown as dashed lines.

ammonia solution (1:1 *v/v*, 10 ml), with stirring for *ca* 30 min, and ethylenediamine (1 mmol, 60 mg) was added to obtain a clear solution. After allowing the solution to stand in air for 10 d, large colourless prism-shaped crystals were formed. The crystals were isolated, washed twice with water and dried in a vacuum desiccator using CaCl$_2$ (yield 63%). Analysis found: C 26.16, H 3.72, N 13.80%; calculated for C$_{11}$H$_{24}$Ag$_2$N$_5$O$_4$: C 26.12, H 4.78, N 13.84%.

Crystal data

[Ag$_2$(C$_2$H$_8$N$_2$)$_3$]- [Ag$_2$(C$_8$H$_{10}$N$_2$O$_3$)$_2$]·2H$_2$O	$Z = 1$
$M_r = 1012.18$	$D_x = 1.943$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.696$ (2) Å	Cell parameters from 3574
$b = 10.759$ (2) Å	reflections
$c = 10.900$ (2) Å	$\theta = 4.3–28°$
$\alpha = 100.54$ (3)°	$\mu = 2.29$ mm^{-1}
$\beta = 99.51$ (3)°	$T = 293$ (2) K
$\gamma = 96.76$ (3)°	Prism, colourless
$V = 864.9$ (4) Å^3	0.15 × 0.08 × 0.04 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2973 independent reflections
φ and ω scans	2102 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.048$
	$\theta_{max} = 25.0°$
$T_{min} = 0.725$, $T_{max} = 0.914$	$h = -9 \rightarrow 4$
3574 measured reflections	$k = -12 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.092P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.152$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.94$	$\Delta\rho_{max} = 1.28$ e Å^{-3}
2973 reflections	$\Delta\rho_{min} = -1.43$ e Å^{-3}
203 parameters	Extinction correction: *SHELXTL*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0173 (18)

Table 1
Selected geometric parameters (Å, °).

Ag1—N3	2.183 (7)	Ag2—N5	2.125 (6)
Ag1—N1	2.277 (8)	Ag3—N4	2.118 (6)
Ag1—N2	2.339 (8)		
N3—Ag1—N1	144.5 (3)	N1—Ag1—N2	76.7 (3)
N3—Ag1—N2	138.8 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$C\cdots$O1W	0.90	2.48	3.168 (11)	134
N2—H2$C\cdots$O1[i]	0.90	2.57	3.311 (10)	141
N2—H2$D\cdots$O2[ii]	0.90	2.20	3.082 (10)	165
N3—H3$C\cdots$O3[iii]	0.90	2.32	3.021 (9)	135
N3—H3$D\cdots$O1[iv]	0.90	2.15	3.012 (10)	161
O1W—H1$WA\cdots$O2[v]	0.84	1.94	2.785 (8)	176
O1W—H1$WB\cdots$O1[vi]	0.84	2.11	2.825 (8)	143

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $x, y, 1+z$; (iii) $x-1, y, z$; (iv) $-x, 2-y, 1-z$; (v) $-x, 1-y, -z$; (vi) $x, y-1, z$.

H atoms of the water molecules were located in a difference Fourier map and were refined with the O—H and H$\cdots$H distances restrained to 0.84 (1) and 1.37 (2) Å, respectively. All other H atoms were placed in idealized positions (N—H = 0.90 Å and C—H = 0.96 or 0.97 Å) and allowed to ride on their parent atoms. The U_{iso}(H) values were set at $1.5U_{eq}$(parent atom) for methyl and water H atoms and $1.2U_{eq}$(C) for all others. At the end of the refinement, the highest peak in the electron-density map was 1.04 Å from Ag2 and the deepest hole was 0.96 Å from Ag2.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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