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Short Communication

A polymeric silver(I) complex containing triply carboxylato-*O*,*O'*-bridged dinuclear cores, $[\{Ag_4(Me_3NCH_2CO_2)_6\}_n](ClO_4)_{4n}$

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Abstract

The title complex consists of discrete perchlorate ions and stepwise one-dimensional cationic chains based on a centrosymmetric tetranuclear sub-unit in which two independent silver(I) atoms are triply bridged by *syn–syn* carboxylato-*O*,*O'* groups of three $Me_3N^+CH_2CO_2^-$ ligands to form a dinuclear core.

Introduction

Most structurally characterized silver(I) carboxylates are composed of either discrete dimers or polymeric systems constructed by the linkage of dimeric sub-units in which each pair of adjacent metal atoms is doubly bridged by coplanar *syn–syn* μ-carboxylato-*O*,*O'* groups [1, 2]. These dimeric structures, formulated as $[Ag_2(\text{carboxylato-}O,O')_2]_n$ (n = 1, 2, or ∞), have been classified into four principal types (see Fig. 1 in ref. 4). Only three exceptions have been reported hitherto. The first is a one-dimensional polymeric arrangement of linear O–Ag–O bonds as found in silver(I) (4-chloro-2-methylphenoxy)acetate [3], where the bridging carboxylato group acts in the *syn–anti* mode. The second is a one-dimensional polymeric structure in which each pair of adjacent metal atoms is bridged by a single *syn–syn* carboxylato-*O*,*O'* group as found in $[\{Ag(C_5H_5N^+CH_2CO_2^-)(NO_3)\}_n]$ [4], and the third is composed of a zigzag chain featuring an uncommon $[\{Ag_2(\text{carboxylato-}O,O')(\text{carboxylato-}\mu\text{-}1,1\text{-}O)\}]$ six-membered ring as found in $[Ag\{C_5H_4(COO)N^+CH_2CO_2^-\}]_n \cdot nH_2O$ [5].

As betaines are structural analogues of the corresponding carboxylate anions, we have taken advantage of their overall charge neutrality to prepare a variety of water-soluble silver(I) betaine complexes [2, 4, 5] and mercury(II) chloride betaine adducts [6]. All these silver(I) complexes were prepared by reacting a silver(I) salt with the corresponding betaine ligand. The use of excess betaine had no effect on the 1:1 metal–ligand molar ratio in the resulting complex, although we have previously established a 1:4 copper(II) betaine complex, $[Cu(Me_3NCH_2CO_2)_4](NO_3)_2$, in which the Cu(II) atom is uncommonly eight-coordinated [7]. Repeated attempts employing various betaines (in excess) and counter anions eventually led to the preparation of the title silver(I) complex with a Ag(I)–betaine molar ratio of 2:3, namely $[\{Ag_4(Me_3NCH_2CO_2)_6\}_n](ClO_4)_{4n}$.

Experimental

The title complex was simply prepared by mixing $AgClO_4$ (0.541 g, 2.61 mmol) and excess betaine ($Me_3N^+CH_2CO_2^-$; IUPAC name: trimethylammonioacetate) monohydrate (0.706 g, 5.52 mmol) in distilled water (10 cm^3) with stirring. After the resulting colourless solution was allowed to stand at room temperature for about three weeks, colourless needle-shaped crystals suitable for X-ray work were obtained.

Crystal data: $Ag_4(C_3H_9NCH_2CO_2)_6 \cdot 4(ClO_4)$, M_r = 1532.8, monoclinic, space group $P2_1/c$ (*No.* 14), a = 5.9341(4), b = 17.501(2), c = 25.919(4) Å, β = 92.08(1)°, U = 2690.0(5) Å^3, Z = 2, $F(000)$ = 1536, T = 295 K, D_{meas} = 1.892 g cm^{-3} ($CCl_4/BrCH_2CH_2Br$), D_{calc} = 1.891 g cm^{-3}, μ(Mo Kα) = 17.1 cm^{-1}.

Intensity data were measured on a Nicolet R3m/V diffractometer with Mo Kα radiation (λ = 0.71073) using the ω-scan technique and corrected for absorption by fitting φ-scan data to a pseudo-ellipsoid [8]. The structure was solved by Patterson superposition. Except for the oxygen atoms in the two-fold disordered perchlorate groups, all non-hydrogen atoms were refined anisotropically, and all H atoms were generated geometrically (C–H = 0.96 Å) and included in structure-factor calculations with assigned isotropic thermal parameters. Convergence was reached at R_F = 0.070 and R_{wF^2} = 0.097 for 3858 observed data ($I > 4\sigma(I)$, $2\theta_{max}$ = 50°) using the weighting scheme $[\sigma^2(|F_o|)+0.0004|F_o|^2]^{-1}$. Computations were performed using the SHELXTL-PLUS program package [9]. Analytic expressions of neutral-atomic scattering factors were used, and anomalous dispersion corrections were incorporated [10]. The final positional parameters and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in

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Table 1, and selected bond lengths and angles in Table 2.

Results and discussion

The title complex comprises discrete perchlorate anions and stepwise one-dimensional cationic chains based on tetranuclear sub-units as shown in Fig. 1. In this sub-unit, two independent silver(I) atoms are *triply* bridged by *syn–syn* carboxylato-*O*,*O*′ groups of three betaine ligands into a dinuclear core with an intra-core metal–metal separation of Ag···Ag = 2.845(1) Å, which is comparable to both the intra-dimeric separation found in a number of silver(I) carboxylates and that in metallic silver (2.89 Å). The three carboxylato groups are arranged in a T-shaped configuration: two approximately coplanar carboxylato-*O*,*O*′ groups bridge two metal atoms in a fashion similar to that in the dimeric structure of silver(I) carboxylates [1, 2] and the third, being nearly perpendicular to the former plane, can be considered

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Ag(1)	−545(1)	1178(1)	528(1)	48(1)
Ag(2)	3582(1)	350(1)	560(1)	44(1)
O(1)	296(9)	1183(3)	−336(2)	48(2)
O(2)	2846(8)	253(3)	−307(2)	39(2)
C(1)	1767(11)	795(4)	−526(2)	31(2)
C(2)	2415(12)	974(4)	−1077(2)	34(2)
N(1)	3798(9)	1693(3)	−1110(2)	32(2)
C(3)	2432(16)	2385(5)	−1008(4)	68(4)
C(4)	5750(14)	1659(5)	−738(3)	62(3)
C(5)	4710(16)	1738(5)	−1648(3)	61(3)
O(3)	−270(10)	666(3)	1360(2)	57(2)
O(4)	3228(11)	221(3)	1412(2)	62(2)
C(6)	1484(14)	497(4)	1589(3)	39(2)
C(7)	1438(12)	647(5)	2169(3)	45(3)
N(2)	3631(10)	815(4)	2451(2)	45(2)
C(8)	4797(17)	1465(5)	2206(4)	75(4)
C(9)	5162(16)	130(5)	2479(4)	66(3)
C(10)	3068(17)	1007(7)	2993(3)	89(4)
O(5)	2471(9)	2202(3)	663(3)	63(2)
O(6)	5629(9)	1537(3)	575(2)	56(2)
C(11)	4545(13)	2139(4)	641(3)	41(2)
C(12)	6121(12)	2842(4)	686(3)	44(2)
N(3)	4998(10)	3600(3)	731(2)	37(2)
C(13)	6875(14)	4183(4)	766(4)	60(3)
C(14)	3682(15)	3663(5)	1217(3)	54(3)
C(15)	3514(15)	3773(5)	272(3)	58(3)
Cl(1)	−636(4)	3272(1)	2325(1)	65(1)
O(7)	1017(23)	2706(8)	2292(7)	120
O(8)	−2973(16)	3067(9)	2231(7)	120
O(9)	−574(29)	3674(9)	2822(4)	120
O(10)	−300(29)	3911(7)	1970(5)	120
O(7′)	−408(28)	2656(7)	2701(5)	120
O(8′)	−412(29)	2840(8)	1834(4)	120
O(9′)	1100(22)	3821(8)	2335(7)	120
O(10′)	−2951(16)	3508(9)	2301(7)	120
Cl(2)	1635(4)	6051(1)	921(1)	57(1)
O(11)	299(26)	5401(7)	1018(7)	120
O(12)	3988(16)	5845(10)	851(7)	120
O(13)	886(28)	6485(10)	472(5)	120
O(14)	1713(39)	6570(11)	1357(6)	120
O(11′)	−725(16)	5844(10)	869(7)	120
O(12′)	1907(38)	6512(12)	1382(6)	120
O(13′)	3345(23)	5520(8)	845(7)	120
O(14′)	1801(29)	6628(9)	501(6)	120

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 2. Selected bond lengths (Å) and bond angles (°)

Ag(1)...Ag(2)	2.845(1)	Ag(1)–O(1)	2.312(5)
Ag(1)–O(3)	2.336(5)	Ag(1)–O(5)	2.548(5)
Ag(1)–O(6d)	2.363(6)	Ag(2)–O(2)	2.280(5)
Ag(2)–O(4)	2.240(5)	Ag(2)–O(6)	2.406(5)
Ag(2)–O(2a)	2.476(5)		
O(1)–Ag(1)–O(3)	152.3(2)	O(1)–Ag(1)–O(5)	87.4(2)
O(3)–Ag(1)–O(5)	96.8(2)	O(1)–Ag(1)–O(6d)	106.9(2)
O(3)–Ag(1)–O(6d)	95.1(2)	O(5)–Ag(1)–O(6d)	118.5(2)
O(2)–Ag(2)–O(4)	160.7(2)	O(2)–Ag(2)–O(6)	99.2(2)
O(4)–Ag(2)–O(6)	97.8(2)	O(2)–Ag(2)–O(2a)	81.0(2)
O(4)–Ag(2)–O(2a)	109.2(2)	O(6)–Ag(2)–O(2a)	86.3(2)
Ag(1)–O(1)–C(1)	124.8(4)	Ag(2)–O(2)–C(1)	117.5(4)
Ag(2)–O(2)–Ag(2a)	99.0(2)	C(1)–O(2)–Ag(2a)	128.6(4)
Ag(1)–O(3)–C(6)	125.0(5)	Ag(2)–O(4)–C(6)	115.7(5)
Ag(1)–O(5)–C(11)	128.7(5)	Ag(2)–O(6)–C(11)	117.9(5)
Ag(2)–O(6)–Ag(1b)	104.7(2)	C(11)–O(6)–Ag(1b)	137.1(5)
O(1)–C(1)	1.224(8)	O(2)–C(1)	1.266(8)
O(3)–C(6)	1.217(9)	O(4)–C(6)	1.245(10)
O(5)–C(11)	1.239(9)	O(6)–C(11)	1.249(9)
O(1)–C(1)–O(2)	126.2(6)	O(3)–C(6)–O(4)	128.5(7)
O(5)–C(11)–O(6)	126.8(7)		

Symmetry codes: (a) $1-x, -y, -z$; (b) $1+x, y, z$; (c) $-x, -y, -z$; (d) $2-x, -y, -z$; (e) $-1+x, y, z$.

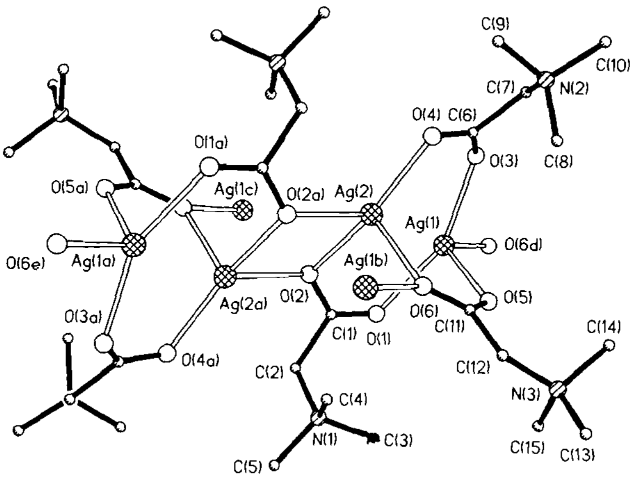
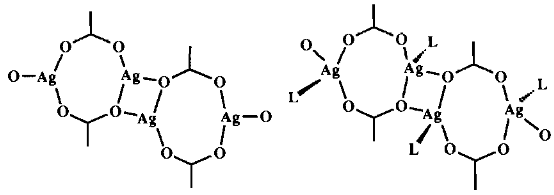


Fig. 1. Perspective view showing the coordination geometry about the metal atoms in $[\{Ag_4(Me_3NCH_2CO_2)_6\}_n](ClO_4)_{4n}$ and the atom numbering scheme. Symmetry codes: (a) $1-x, -y, -z$; (b) $1+x, y, z$; (c) $-x, -y, -z$; (d) $-1+x, y, z$; (e) $2-x, -y, -z$.

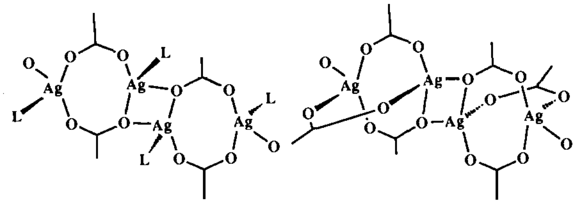
as the replacement of two *syn*-related axial ligands (L) in a modified type **D**$_2$ dimeric structure (Fig. 2) as found in $[\{Ag_2(C_5H_5N^+CH_2CH_2CO_2^-)_2(NO_3)_2\}_n]$ (L = *O*-NO_2) [2c]. In the present core the metal atoms are each in a highly distorted tetrahedral environment with Ag–O bonds ranging from 2.240(5) to 2.548(5) Å and O–Ag–O bond angles from 86.3(2) to 160.7(2)°. Large distortion from regular coordination geometry has also been found in a trigonally coordinated Ag(I) carboxylate [4].

The three independent betaine ligands in the present complex function in different ways. Although all act as *syn–syn* bridging ligands to form the dinuclear core, one of them also connects the two cores via metal–carboxylate linkages of the type Ag(2)–O(2a) (2.476(5) Å) into a tetranuclear sub-unit, generating a centrosymmetrical Ag_2O_2 rhomb as found in the dimer-based polymeric silver(I) carboxylates; a second betaine further links the sub-units by metal–carboxylate linkages (Ag(1)–O(6d) 2.363(3) Å) into a stepwise one-dimensional cationic chain running parallel to the *a*-axis in the unit cell.

The triple carboxylato-*O*,*O*′ bridges in the dinuclear core make the structure of the title complex distinct from those of all the other structurally characterized silver(I) carboxylates, for which bis(carboxylato-*O*,*O*′)-bridged dimeric species predominate. Hitherto there is no record of polymeric metal complexes based on similar tetranuclear sub-units in the literature. Although a novel triply (carboxylato-*O*,*O*′)-bridged linear polymeric complex, $[Mn(Me_3NCH_2CO_2)_3]_n \cdot nMnCl_4$, has recently been reported [10], the C_3-related triple carboxylato-*O*,*O*′ bridges in it function in an uncommon skew–skew mode that is very different from the T-shaped configuration found in the title complex.



(a) Type **D**. (b) Modified type **D**$_1$.



(c) Modified type **D**$_2$. (d) Triply bridged dinuclear cores in the tetranuclear sub-unit.

Fig. 2. Triply carboxylato-*O*,*O*′-bridged dinuclear cores in the tetranuclear sub-unit of $[\{Ag_4(Me_3NCH_2CO_2)_6\}_n](ClO_4)_{4n}$ (d) and the related bis(carboxylato-*O*,*O*′)-bridged dimeric structures (a)–(c).

Supplementary material

Additional material comprising the remaining bond lengths and angles, thermal parameters, H-atom coordinates, and observed and calculated structure-factor amplitudes (22 pages) are available from author T.C.W.M. on request.

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