Crystal Structure of Silver(I) Glutarate, a Two-dimensional Polynuclear Coordination Polymer

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Silver(I) glutarate is a 2D polynuclear polymer whose repeat unit consists of a tetranuclear silver cluster coordinated by two bridging glutarate anions; these units are organised, through additional metal–oxygen linkages, in layers parallel to the *ac* plane, in which uncommon metal–metal contacts (3.14–3.43 Å) are observed.

Linking metallic cations with appropriate multi-dentate ligands is a promising method for obtaining new solid-state materials with possible applications in solid-state technology.[1] Using this approach a number of one-,[2] two-[3] and three-dimensional[4] infinite frameworks have recently been described. In this context, we investigate the potential of α,ω-dicarboxylic acids as building units and we recently employed silver(I) for connecting succinate anions. Crystal structure analysis[5] showed that the organic units were linked by tetranuclear silver clusters forming a 3D diamondoid network. In this work we describe a 2D polynuclear silver(I) coordination polymer, presenting some unique structural features. In addition, short metal–metal contacts (inferior or close to twice the van der Waals radius of silver, 3.44 Å[6]) are observed within the layers.

Crystals of $[Ag_4\{OOC\text{-}(CH_2)_3\text{-}COO\}_2]$ **1** were prepared as follows: an aqueous solution of 10 ml of glutaric acid (0.05 mol dm^{-3}) was slowly neutralized, under vigorous stirring, by a sodium silicate solution (d = 1.06) up to pH 6. The resulting gelling solution was introduced into a test tube and was allowed to stand for 24 h. Then, 10 ml of an aqueous solution of $AgNO_3$ (0.05 mol dm^{-3}) was carefully added at the top of the gel.[7–8] Thin prismatic crystals, almost colourless (very pale violet), were formed in the gel, at ambient temperature, within three days. The material is insoluble in water as well as in common organic solvents. Its stoichiometric formula is based on crystal structure results. X-Ray diffraction† shows that the structure consists of $Ag_4(Glut)_2$, (Glut = glutarate), repeat units held together by weak 'lateral' silver–carboxylate linkages. In addition, the structure is probably further stabilised by short 'intermolecular' metal–metal contacts extending in both the *a* and *c* directions.

Fig. 1 shows the molecular structure of **1**. This unusual building unit, of point symmetry C_i, consists of an aggregate of four silver(I) atoms, arranged around a crystallographic inversion centre and 'clamped' by two bridging glutarate anions. A key element for obtaining this unit is the bound conformation of the two ligands. Both of them adopt a *gauche–gauche* conformation which is not the lowest energy one for dicarboxylic acids. Coordination distances and angles in the eight-membered ring are similar to previously reported values for complexes of silver with carboxylic acids.[9] Each tetranuclear repeat unit is linked to four neighbouring units through additional metal–carboxylate oxygen interactions. The resulting rhombic Ag_2O_2 units run in a zig-zag fashion in a direction parallel to the *c* axis (Figs. 2, 3). The polymeric layers formed in this way are parallel to the *ac* plane. Coordination distances in Ag_2O_2 are shown in Fig. 3. Although the distances Ag(2)–O(2) (2.75 Å) and Ag(1)–O(1) (2.77 Å) are somewhat long (the sum of the ionic radii is 2.67 Å) the regularity of the structure suggests that there must be some weak interaction.

The intra-unit metal–metal distances of 3.20 and 3.42 Å (Fig. 1) are within the range of weak nonbonded interactions. The distance of 2.80 Å observed between the pair of silver atoms in the eight-membered ring is less than that in the metal (2.89 Å) and might indicate a bonded interaction.

The metal–metal distance between silver atom pairs belonging to two neighbouring repeat units in the direction of the *c* axis is 3.14 Å (Figs. 2, 4), well below the van der Waals contact distances and comparable to the metal–metal distance found in many purely inorganic compounds of silver.[10]

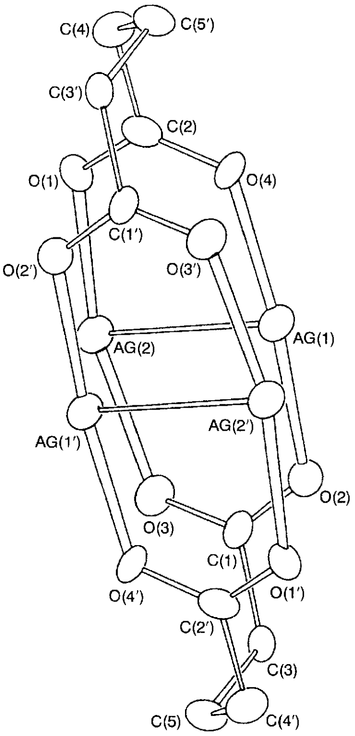

Fig. 1 ORTEP view of the structure of $Ag_4(Glut)_2$. Selected distances (Å). Ag(1)–O(2), 2.161(7); Ag(1)–O(4), 2.107(7); Ag(2)–O(1), 2.304(7); Ag(2)–O(3), 2.223(8); Ag(1)–Ag(2), 2.804(1); Ag(1)–Ag(2′), 3.425(1); Ag(1)–Ag(1′), 3.208(1); Ag(2)–Ag(2′), 3.730(1). Significant angles (°): O(2)–Ag(1)–O(4), 171.0(3); O(1)–Ag(2)–O(3), 157.5(3); Ag(1)–Ag(2)–Ag(1′), 61.0(3).

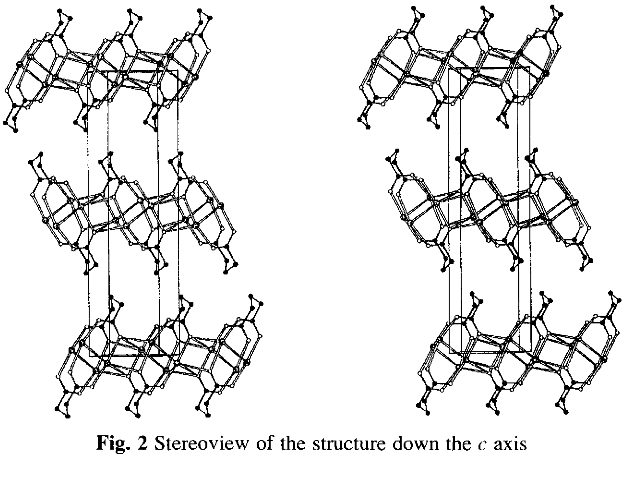

Fig. 2 Stereoview of the structure down the *c* axis

The metallic ribbons, which are thus formed are parallel to *c* and perpendicular to the *b* axis. Short metal–metal contacts are also observed in the *a* axis direction (Fig. 4). In this case only the atoms of Ag(1) type interact with the corresponding atoms of the neighbouring ribbons (3.43 Å), leading to formation of infinite metal layers parallel to the *ac* plane. Although the presence of weak metal–oxygen interactions between neighbouring repeat units undoubtedly contributes to the stabilisation of the structure we estimate that, in this respect, the metal–metal interactions, especially the interunit ones, are probably not negligible. The possible role of d^{10}–d^{10} interactions in the stabilisation of the crystal packing of silver complexes was also invoked recently by Mak *et al.*[11] However, measurement of physical properties of single crystals or computational studies would be necessary to clarify this point.

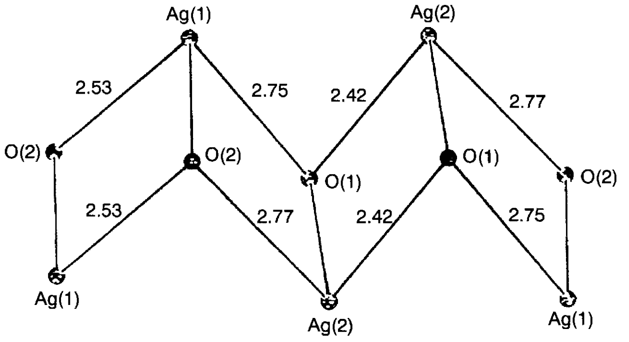

Fig. 3 View of the Ag_2O_2 ribbons running parallel to the *c* axis. Interatomic distances (Å) are indicated.

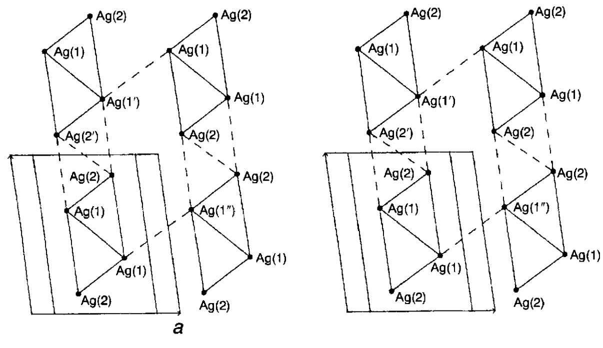

Fig. 4 View of one layer on the *ac* plane. Organic units are omitted for clarity. Selected interunit distances (Å): Ag(2)–Ag(2′), 3.420(1); Ag(2)–Ag(1′), 3.141(1); Ag(1)–Ag(1″), 3.438(1). Dashed lines indicate interunit distances.

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Footnote

† *Crystal data* for **1**: monoclinic, $P2_1/n$, a = 5.024(2), b = 20.724(4), c = 6.498(2) Å, β = 97.29(1)°, V = 671.13 Å^3, Z = 4 (the asymmetric unit is half of the molecule), D_c = 3.424 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, 1640 reflections measured, 969 observed [$I > 3\sigma(I)$], R = 0.035, Rw = 0.038. Data reduction with SDP package. Structure solved by Patterson and Fourier methods. Refinement with SHELX76 and XTAL3.0. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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