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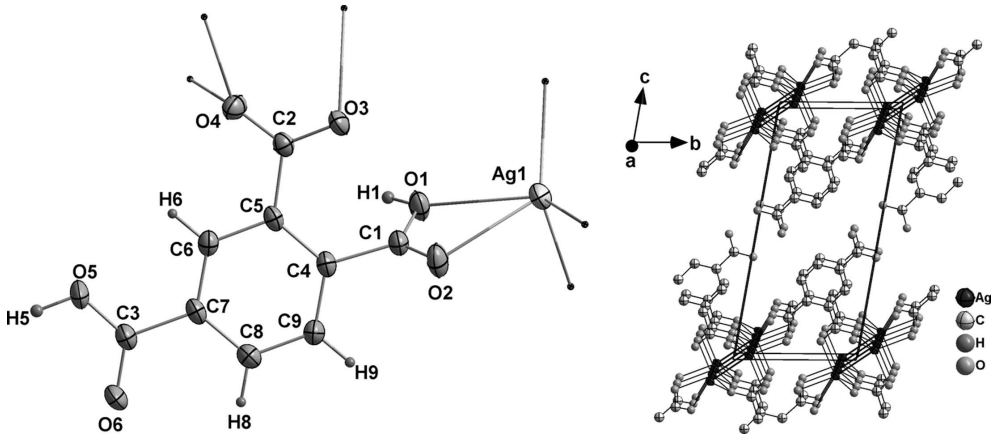
# The crystal structure of poly[($\mu_5$-2,5-dicarboxybenzoato-$\kappa^4O:O:O':O'',O'''$)silver(I)], $C_9H_5AgO_6$

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## Abstract

$C_9H_5AgO_6$, triclinic, $P\bar{1}$ (no. 2), $a = 3.7933(5)$ Å, $b = 7.6762(11)$ Å, $c = 15.534(2)$ Å, $\alpha = 79.109(2)°$, $\beta = 89.864(2)°$, $\gamma = 78.122(2)°$, $V = 434.35(10)$ Å$^3$, $Z = 2$, $R_{gt}(F) = 0.0302$, $wR_{ref}(F^2) = 0.0650$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colourless block |
| Size: | 0.15 × 0.15 × 0.10 mm |
| Wavelength: | Mo $K\alpha$ radiation (0.71073 Å) |
| $\mu$: | 2.33 mm$^{-1}$ |
| Diffractometer, scan mode: | APEX, $\omega$ and $\varphi$ |
| $\theta_{max}$, completeness: | 28.3°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 5417, 2128, 0.029 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 1800 |
| $N(param)_{refined}$: | 145 |
| Programs: | Bruker [1], SHELX [2] |

## Source of material

Single crystal of $C_9H_5AgO_6$ was prepared by the following procedure: a mixture of $AgNO_3$ (0.170 g, 1 mmol), NaOH (0.040 g, 1 mmol), 1,2,4-benzenetricarboxylic acid (0.210 g, 1 mmol) was dissolved in 5 mL deionized water, which was then placed in a 25 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C under autogenously pressure for seven days. After being slowly cooled to room temperature at a rate of 4 °C/h, some colourless block shaped crystals were successfully obtained.

## Experimental details

The H atoms of C atoms were positioned geometrically and refined with a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of carboxyl were located in difference Fourier maps, and then refined with a riding model, with $U_{iso}(H) = 1.2U_{eq}(O)$.

## Comment

In recent years, there has been continuous interest in the design and synthesis of coordination polymers (CPs) and supramolecular architectures due to their potential applications in the fields of magnetism, porous materials, catalysis and nonlinear optical activities or molecular recognition [3–5]. A novel design for CPs be accessed

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**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ag1 | 0.52766(8) | 0.13914(4) | 0.05272(2) | 0.03197(10) |
| C1 | 0.1709(9) | 0.3892(4) | 0.1705(2) | 0.0244(7) |
| C2 | 0.2086(8) | 0.7882(4) | 0.1290(2) | 0.0208(6) |
| C3 | −0.3108(9) | 0.8489(4) | 0.4192(2) | 0.0263(7) |
| C7 | −0.1749(8) | 0.7321(4) | 0.3548(2) | 0.0223(6) |
| C8 | −0.1754(9) | 0.5479(4) | 0.3748(2) | 0.0254(7) |
| H8 | −0.255444 | 0.497366 | 0.428542 | 0.030* |
| C9 | −0.0558(9) | 0.4400(4) | 0.3140(2) | 0.0262(7) |
| H9 | −0.053271 | 0.316402 | 0.327250 | 0.031* |
| C4 | 0.0602(8) | 0.5157(4) | 0.2334(2) | 0.0208(6) |
| C5 | 0.0663(8) | 0.7005(4) | 0.21293(19) | 0.0200(6) |
| C6 | −0.0532(8) | 0.8075(4) | 0.2747(2) | 0.0225(6) |
| H6 | −0.051650 | 0.930720 | 0.262117 | 0.027* |
| O1 | −0.0180(7) | 0.4186(3) | 0.09627(15) | 0.0312(5) |
| H1 | −0.207219 | 0.510994 | 0.090397 | 0.037* |
| O2 | 0.4203(7) | 0.2610(3) | 0.18744(16) | 0.0356(6) |
| O3 | 0.4109(6) | 0.6909(3) | 0.08416(14) | 0.0270(5) |
| O4 | 0.1181(6) | 0.9585(3) | 0.10780(16) | 0.0298(5) |
| O5 | −0.2776(8) | 1.0133(3) | 0.40087(17) | 0.0443(7) |
| H5 | −0.357308 | 1.083293 | 0.441585 | 0.053* |
| O6 | −0.4527(8) | 0.7827(3) | 0.48714(16) | 0.0392(6) |

by many factors, including the metal/ligand stoichiometry, temperature, pH value, solvents and the type of counterion used during the preparation process. The selection of suitable organic ligands are crucial for constructing extended coordination frameworks. As one of the most fascinating ligands, 1,2,4-benzenetricarboxylic acid ($H_3BTC$) is selected as a cluster ligand because its three carboxylate groups may be completely or partially deprotonated, and can act as hydrogen bond acceptors as well as hydrogen bond donors to assemble supramolecular structures. Up to now, many reports have been produced based on $H_xBTC$ (x = 0–3) ligands, such as $[Cd(H_2O)(1,2,4\text{-HBTC})(ppene)_{0.5}]_n$ [6], $[Ni_3(BTC)_2(bpp)_2(H_2O)]\cdot 3H_2O$ [7], $CsNi_3(OH)(H_2O)_3(BTC)_2\cdot 3H_2O$ [8], and so on. On the other hand, the silver(I) ion, with a closed-shell ($d^{10}$) outer electronic configuration, has been known as a good central atom in CPs because of their variable coordination number, flexible geometry and good physical properties. Moreover, silver(I) ions have a strong trend to form polynuclear species through Ag—Ag bonds. Until now, a large number of mono-, di- and tetranuclear Ag-complexes have been reported in the literature, such as $\{[Ag_2(4\text{-pyf})_2]\cdot THF\}_n$ [9], $[Ag(bpa)_2(CF_3SO_3)(H_2O)]_n$ [10] and $[Ag_4(PPh_3)_4(AMP)_2(NO_3)_4]_n$ [11]. Interestingly, 1D infinite Ag(I) wire was found in the cavities of CP compounds, which was then attracted much attention for their potential applications as molecular wires and molecular electronic devices [12–14]. Such a structure was sustained by ligand-unsupported Ag—Ag contacts with the distances of 2.9 ∼ 3.2 Å.

This work provided a new CP, $Ag(H_2BTC)$, its synthesis and the crystal structure determination. Single-crystal X-ray diffraction analysis revealed that there is a unique $H_2BTC^-$ ligand and a unique one $Ag^+$ ion in each asymmetric unit. The title compound $Ag(H_2BTC)$ features a two-dimensional (2D) supramolecular layered structure that is constructed interlinked by Ag—O bonds and O—H···O hydrogen bonds. In this structure, all $Ag^+$ ions are linked to each other through argentophilic interactions to produce $\{Ag_2\}$ dimers with the Ag—Ag distances of 2.9661(6) Å, which is close to the Ag—Ag contacts in the metallic silver [15], and is shorter than Ag—Ag distances in other reported polynuclear silver(I) CPs $[Ag(Diaz)_2Ag(CN)_2]$ (3.12 Å) [16] and $[Ag_2(H_2bptc)(bpp)_2]_n$ (3.176 Å) [17]. Thus we confirm that a strong Ag—Ag metalic bond is formed here. Then a $\{Ag_2\}$ dimer is surrounded by ten O atoms from six carboxyl groups of $H_2BTC^-$, as shown in the right part of the figure. Notice that each $Ag^+$ ion is coordinated by five $O^{2-}$ ions with the Ag—O bond distances of 2.313(2) ∼ 2.449(2) Å. The $H_3BTC$ ligands in the structure are partially deprotonated containing an interior hydrogen bond, noted as $H_2Btec^{2-}$. Both protonated and deprotonated carboxyl groups conntect with $Ag^+$ ions through Ag—O bonds (*cf.* left part of the figure): the only deprotonated carboxyl group connects to three $Ag^+$ ions, a protonated carboxyl group connects one $Ag^+$ ion, and the rest undeprotonated carboxyl group is not connected by $Ag^+$ ions. The Ag—O bond distances fall in the range of 2.313(2) ∼ 2.449(2) Å. It is apparent that the inorganic part of title compoud is $Ag_2O_7$ units, which are further linked to each other to form a infinite 1D chain along the *a* axis. Viewing along this direction, the $\{Ag_2\}$ dimers are in ordered rows and are seperated by organic ligands to form a 2D layer. This result indicates that the Ag—Ag contact is largely supported by ligands. Furthermore, the 2D layers are stacking running along the *c* axis, in a way that all ligands point to the outer space of each layer, as shown in the right part of the Figure. It is worthy mentioned that the O5—H5···O6 hydrogen bonds play an important role in the connection of neighbouring layers. Within the other CP compound $[Ag_3(1,2,4\text{-BTC})]_n$ that is constructed by $Ag^+$ ion and $H_3BTC$ ligand, all carboxyl groups are deprotonated and provide more coordination O atoms with $Ag^+$ ions ($\mu_{11}$) to generate a complicated 3D framework [18]. We may predict that more CPs with interesting structures will be found containing $Ag^+$ ion and $H_3BTC$ ligand in the future.

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## References

1. Bruker. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2009).
2. Sheldrick, G. M.: SHELXT-integrated space-group and crystal structure determination. Acta Crystallogr. **C71** (2015) 3–8.
3. Zhang, H.-J.: Crystal structure of catena-triaqua(5-methoxyisophthalate)cadmium(II) – water (1:2), $Cd(C_9H_6O_5)(H_2O)_3 \cdot 2H_2O$. Z. Kristallogr. NCS **226** (2011) 629–630.
4. Vologzhanina, A. V.; Avdeeva, V. V.; Malinina, E. A.; Kuznetsov, N. T.: Synthesis and crystal structure of poly (tetraphenylphosphonium ($\mu_2$-closo-decaborato)copper(I)). Z. Kristallogr. **228** (2013) 565–569.
5. Xu, H.; Zheng, H.-G.: Syntheses, crystal structures and properties of two new compounds from a flexible bipodal acid with additional amide groups. Chin. J. Struct. Chem. **36** (2017) 1034–1042.
6. Li, N.-Y.; Ma, W.; Wang, S.-J.; Liu, D.: Effect of substituent carboxylic group on the self-assembly of cadmium coordination polymers: syntheses, topological analyses and photoluminescence properties. Inorg. Chem. Commun. **58** (2015) 1–4.
7. Wang, J. L.; Bai, Y.; Pan, H.; Zheng, G. S.; Dang, D. B.: Long-range magnetic ordering in a metal-organic framework based on octanuclear nickel(II) clusters. Dalton Trans. **46** (2017) 12771–12774.
8. Peng, Y. R.; Chien, P. H.; Chung, H. T.; Pan, P. Y.; Liu, Y. H.; Yang, E. C.: Studies of the structural and magnetic properties of an unsymmetrical ligand 1,2,4-benzenetricarboxylic acid based chiral 3-D trinickel coordination polymer as an alkali base-influenced hydrothermal reaction product. J. Solid State Chem. **212** (2014) 159–164.
9. Hsu, W.; Yang, X.-K.; Mahat Chhetri, P.; Lin, S.-J.; Li, Y.-S.; Chen, T.-R.; Chen, J.-D.: Au(I) and Ag(I) formamidinate tetranuclear complexes and coordination polymers: synthesis, structures and luminescent properties. Inorg. Chim. Acta **482** (2018) 785–790.
10. Yuan, Y.; Xue, X.-N.; Fan, W.-W.; Qiu, Q.-M.; Cui, Y.-Z.; Liu, M.; Li, Z.-F.; Jin, Q.-H.; Yang, Y.-P.; Zhang, Z.-W.; Geng, W.-X.; Zheng, W.-J.: Effect of solvent on the architectures of six Ag(I) coordination polymers based on flexible and quasi-flexible organic nitrogen donor ligands. Polyhedron **106** (2016) 178–186.
11. Cui, L.-N.; Hu, K.-Y.; Jin, Q.-H.; Li, Z.-F.; Wu, J.-Q.; Zhang, C.-L.: Polynuclear silver(I) complexes of triphenylphosphine and 2-aminopyrimidine: synthesis, structural characterization and spectroscopic properties. Polyhedron **30** (2011) 2253–2259.
12. Chisholm, M. H.; Patmore, N. J.: Studies of electronic coupling and mixed valency in metal-metal ouadruply bonded complexes linked by dicarboxylate and closely related ligands. Acc. Chem. Res. **40** (2007) 19–27.
13. Xiong, K.; Wu, M.; Zhang, Q.; Wei, W.; Yang, M.; Jiang, F.; Hong, M.: 1D infinite silver (I) chains reside in the big cavities built by the novel p-sulfonatocalix[4]arenetrisilver blocks. Chem. Commun. (2009) 1840–1842.
14. Liu, F.-J.; Sun, D.; Hao, H.-J.; Huang, R.-B.; Zheng, L.-S.: A novel photoluminescent silver(I) wire supported by 4-tert-butylbenzoate and ligand-unsupported Ag-Ag interactions. Inorg. Chem. Commun. **15** (2012) 136–139.
15. Vegard, L.: Structure of silver crystals. Philos. Mag. **31** (1916) 83–87.
16. Espinosa Ferao, A.; Afzal, F.; Aslam, S.; Muhammad, I. K.; Ejaz; Khan, I. U.; Fettouhi, M.; Isab, A. A.; Ahmad, S.: Synthesis, crystal structure and DFT calculations of bis(1,3-diazinane-2-thione-κ*S*)dicyanido disilver(I), $[\{Ag(Diaz)_2\}\{Ag(CN)_2\}]$. Polyhedron **110** (2016) 299–304.
17. Zhang, Y.-N.; Wang, H.; Liu, J.-Q.; Wang, Y.-Y.; Fu, A.-Y.; Shi, Q.-Z.: Novel silver(I) compounds assembled from hybrid ligands based on linear or T-shaped coordination environment. Inorg. Chem. Commun. **12** (2009) 611–614.
18. Chen, Q.; Lun, H. J.; Li, Y. H.; Li, S.; Li, B. B.; Zhang, X. D.; Li, Y. M.: Hydrothermal synthesis and structural characterization of a three-dimensional coordination oolymer on Ag(I). Synth. React. Inorg. Met.-Org. Nano-Met. Chem. **46** (2016) 730–734.