DALTON
COMMUNICATION

A novel luminescent 3D polymer containing silver chains formed by ligand unsupported Ag–Ag interactions and organic spacers†

Daofeng Sun, Rong Cao,* Jiabao Weng, Maochun Hong* and Yucang Liang

State Key Laboratory of Structural Chemistry, Fujian Institute of the Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou, 350002, China.
E-mail: hmc@ms.fjirsm.ac.cn

Received 15th November 2001, Accepted 19th December 2001
First published as an Advance Article on the web 10th January 2002

A luminescent polymer $[\{Ag(H_2btc)_2\}\{Ag_2(Hbtc)\}]_n$ with weak semiconductivity has been synthesized; structural analysis shows that the polymer possesses a 3D structure which contains silver chains formed by ligand unsupported Ag–Ag interactions and carboxylate spacers.

Recently, the fascinating properties of polymeric silver complexes have attracted increasing interest from chemists, and the presence of different Ag–Ag interactions has been proven to be one of the most important factors contributing to such properties. For instance, the silver cyanurate polymer $[Ag_2C_3N_3HO_3]_n$, comprised of silver sheets, possesses anisotropic conductivity[1] and the silver thiolate polymer $[Ag(C_5H_4NS)]_n$, which has graphite-like Ag_6 motifs, shows semiconductivity.[2] However, many Ag–Ag interactions in reported complexes are ligand-supported, *e.g.* the silver ion geometry is maintained by bridging or capping ligands; the interactions formed by d^{10}–d^{10} metal–metal attraction, *e.g.* ligand-unsupported Ag–Ag interactions, are scarce, and only a few examples have been reported in the literature.[3–9] As already known, benzoic multicarboxylate ligands are versatile building blocks for the construction of polymeric structures,[10] for example, the use of benzene-1,3,5-tricarboxylate (btc^{3-}) has resulted in many interesting complexes.[10,11] Surprisingly, studies on silver benzoic multicarboxylate polymers have received less consideration[12] because they often appear as insoluble salts that make structural analyses difficult. In this communication, we will report a novel 3D silver(I) polymer, $[\{Ag(H_2btc)_2\}\{Ag_2(Hbtc)\}]_n$ (**1**), which is constructed of silver chains formed by ligand unsupported Ag–Ag interactions and H_2btc^- and $Hbtc^{2-}$ spacers. We will show that the presence of silver chains in **1** results in interesting semiconductivity and photoluminescence properties.

Slow diffusion of a MeOH solution of $AgNO_3$ into an aqueous solution of H_3btc yielded **1** as colorless prism crystals.‡ Single crystal structure analysis§ showed that **1** possesses a three-dimensional structure, which comprises two independent building units, $Ag_2(H_2btc)_2$ (A) and $Ag_8(Hbtc)_{12/3}$ (B). In unit A, the deprotonated carboxyl group of H_2btc^- acts as a bridge linking two Ag atoms through its two oxygen atoms, one of the protonated carboxyl groups coordinates to one Ag atom *via* its carbonyl oxygen and the other one remains free. The two Ag atoms in A are bridged by two deprotonated carboxyl groups with an Ag–Ag distance of 2.9762(13) Å. Each two A units are linked together through weak $Ag–O_{carbonyl}$ bonding, completing the distorted trigonal coordination geometry of Ag and yielding a 1D chain structure (Fig. 1). Every two adjacent chains that are aligned in different directions are combined *via* ligand unsupported Ag–Ag interactions [Ag1–Ag1, 2.9626(12) Å], forming a 3D structure.

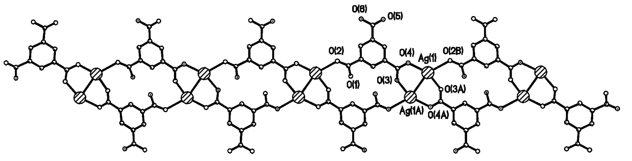

Fig. 1 Structure of the linear chain formed by unit A. Selected bond distances (Å) and angles (°): Ag1–Ag1a, 2.9762(13); Ag1–O2, 2.484(5); Ag1–O3, 2.221(5); Ag1–O4, 2.209(5); O–Ag–O, 82.57(17)–153.84(18).

Unit B is composed of four Ag_2 subunits, each of which is connected by two deprotonated carboxyl groups. Two Ag3–Ag4 subunits [Ag3–Ag4, 3.2104(11) Å] are joined by ligand unsupported Ag–Ag interactions [Ag3–Ag3, 3.0923(16) Å], generating a linear Ag_4 chain, which connects two Ag2–Ag2 [2.9894(13) Å] subunits through weak Ag–O bonding and ligand unsupported Ag–Ag interactions [Ag2–Ag3, 3.1848(6) Å] (Fig. 2). There are three kinds of Ag in B: Ag2, Ag3 and Ag4 are in O_3 distorted trigonal, O_2 linear and O_4 distorted tetragonal geometries, respectively. Interestingly, all Ag4–O bonding is very weak [Ag4–O, 2.505(5)–2.547(5) Å], and Ag4 may be viewed as a "loose" atom dotted in B through Ag–Ag and Ag–O interactions. The protonated carboxyl group of $Hbtc^{2-}$ in B coordinates to one Ag atom through its carbonyl oxygen; one deprotonated carboxyl group links two Ag atoms *via* two oxygen atoms and the other deprotonated oxygen connects three Ag atoms (one oxygen attaches one and the other bridges two Ag atoms). Thus $Hbtc^{2-}$ acts as a μ_6-bridge to link three B units, resulting in another 3D structure. Owing to the ligand unsupported Ag–Ag [Ag1–Ag2, 3.2782(8) Å] interactions between the two kinds of 3D structures they interpenetrate each other, producing linear distorted ladder-like Ag chains (Fig. 3) and the final condensed 3D structure (Fig. 4). The whole structure can also be regarded as parallel Ag chains linked by H_2btc^- and $Hbtc^{2-}$ spacers.

The most intriguing feature of the structure of **1** is the presence of ligand unsupported Ag–Ag interactions, which play an important role in the formation of the complex: the 3D structure constructed by unit A, unit B and the Ag chains in the structure are formed through such interactions. All the ligand unsupported Ag–Ag distances [ranging from 2.9626(12) to 3.2782(8) Å] are shorter than the van der Waals contact distance for Ag–Ag (3.40 Å),[13] the shortest [2.9626(12) Å] is only slightly longer than that found in metallic silver (2.89 Å) and is shorter than other reported ligand unsupported Ag–Ag distances (ranging from 2.987 to 3.655 Å).[3–9] Prior to this communication, only several complexes containing ligand unsupported Ag–Ag interactions have been reported,[3–9] most of them constructed by nitrogen containing ligands, the only two examples containing carboxylate ligands are Ag(I)-aminobenzoato[6] and Ag(I)-betaine derivatives.[9] To the best of our knowledge, complex **1** is the first silver benzoic multicarboxylate polymer containing ligand unsupported Ag–Ag interactions, although some related compounds have already appeared in the literature.[12]

Aside from structural features, evidence of metal–metal interactions in extended solids can also be provided by physical properties.[14] Determination of the conductivity of **1** (powder

---

† Electronic supplementary information (ESI) available: photoluminescence emission spectrum of **1**. See http://www.rsc.org/suppdata/dt/b1/b110436e/

DOI: 10.1039/b110436e

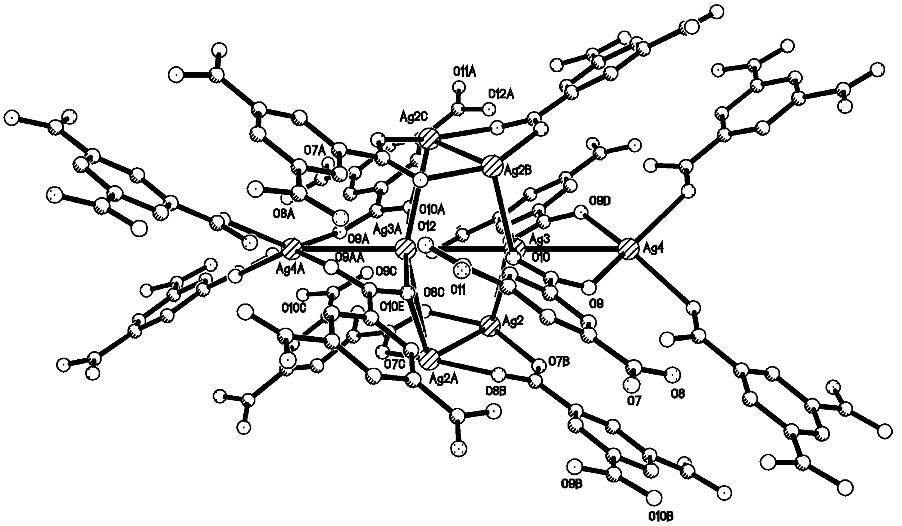

Fig. 2 Structure of unit B. Selected bond distances (Å) and angles (°): Ag–Ag, 2.9894(13)–3.2108(11); Ag2–O7, 2.261(5); Ag2–O8, 2.227(5); Ag2–O10c, 2.560(5); Ag3–O10, 2.109(4); Ag4–O9, 2.547(5); Ag4–O11, 2.505(5); O–Ag2–O, 91.88(16)–154.96(17); O–Ag3–O, 174.8(3); O–Ag4–O, 81.97(15)–145.42(16).

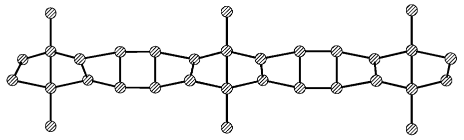

Fig. 3 The structure of the silver chain formed by ligand unsupported Ag–Ag interactions in **1**.

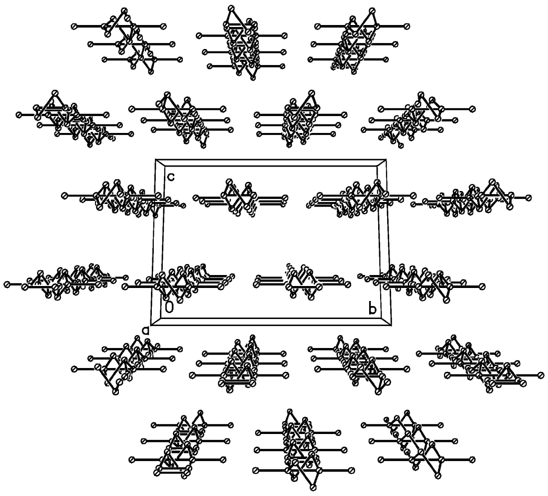

Fig. 4 The packing structure along the *a* axis of **1**. Organic spacers are omitted for clarity.

sample from ground crystals) illustrates a conductivity of 1.06×10^{-6} S cm^{-1} at room temperature, and increases with temperature. This result indicates that **1** possesses semiconducting properties, which may be attributed to the presence of silver chains, but the conductivity is quite weak compared to complexes with silver sheets.[1,2] As known, Ag(I) complexes may emit weak photoluminescence at low temperature, but room temperature examples are scarce.[7,8,15] At room temperature, **1** shows strong blue photoluminescence with an emission maximum at 460 nm upon excitation at 360 nm in the solid state (as powder samples, see ESI).† The observed luminescence of **1** may be assigned as ligand-to-metal charge transfer (LMCT) and an excited state of pure d–s origin modified by metal–metal interaction,[16] although detailed study is still needed. The peaks from 425 to 440 nm may result from the carboxylate ligands.

We are grateful for the financial support from NNSFC and the key project from CAS.

Notes and references

‡ Preparation of [{Ag(H$_2$btc)}{Ag$_2$(Hbtc)}]$_n$ (**1**). A solution of AgNO$_3$ (0.085 g, 0.5 mmol) in MeOH (5 ml) was carefully layered onto an aqueous solution (10 ml) of btc (0.053 g, 0.25 mmol) in a glass tube in the dark. Prism-like crystals were obtained after one week. Yield: 69%. Calc. for C$_{18}$H$_9$Ag$_3$O$_{12}$: C 29.18, H 1.22%; Found: C 29.20, H 1.18%. IR(KBr, cm^{-1}): 3469(vs), 3107(s), 2887(s), 2517(s), 1705(s), 1686(vs), 1610(s), 1564(s), 1275(vs), 931(m), 688(s).

§ Crystal data for **1**. C$_{18}$H$_9$Ag$_3$O$_{12}$, orthorhombic, space group *Fddd*, a = 14.8775(2), b = 25.9261(2), c = 36.3777(2) Å, U = 14031.4(2) Å^3, T = 293 K, Z = 16, D_c = 1.403 g cm^{-3}, λ = 0.71073 Å, 9447 reflections measured, 3094 unique which were used in all calculations. $R1$ = 0.0433 and $wR2$ = 0.1016. CCDC reference number 166791. See http://www.rsc.org/suppdata/dt/b1/b110436e/ for crystallographic data in CIF or other electronic format.

1 C. N. R. Rao, A. Ranganathan, V. R. Pedireddi and A. R. Raju, *Chem. Commun.*, 2000, 39.

2 W. P. Su, M. C. Hong, J. B. Weng, R. Cao and S. F. Lu, *Angew. Chem., Int. Ed.*, 2000, **39**, 2911.

3 O. Kristiansson, *Inorg. Chem.*, 2001, **40**, 5058.

4 M. L. Tong, X. M. Chen, B. H. Ye and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 5278.

5 M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle and H. H. Patterson, *Inorg. Chem.*, 1998, **37**, 1380.

6 K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 1942.

7 B. L. Fei, W. Y. Sun, T. Okamura, W. X. Tang and N. Ueyama, *New J. Chem.*, 2001, **25**, 210.

8 M. L. Tong, X. M. Chen, B. H. Ye and L. N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237.

9 X. M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1991, 3253.

10 (*a*) O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703; (*b*) H. J. Choi and M. P. Suh, *J. Am. Chem. Soc.*, 1998, **120**, 10622; (*c*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *Chem. Commun.*, 1999, 841.

11 (*a*) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*b*) S. O. H. Gutschke, M. Lolinier, A. K. Powell, R. E. P. Winpenny and P. T. Wood, *Chem. Commun.*, 1996, 823; (*c*) C. J. Kepent and M. J. Rosseinsky, *Chem. Commun.*, 1998, 31; (*d*) O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.

12 G. Smith, A. N. Reddy, K. A. Byriel and C. H. L. Kennard, *J. Chem. Soc., Dalton. Trans.*, 1995, 3565.

13 Y. Du, S. R. Wilson, P. Zhang, K. Hirsch and J. S. Moore, *J. Chem. Educ.*, 1997, **74**, 915.

14 Y. J. Zhao, M. C. Hong, Y. C. Liang, R. Cao, W. J. Li, J. B. Weng and S. F. Lu, *Chem. Commun.*, 2001, 1020 and references therein.

15 (*a*) D. H. Pierre and F. Daniel, *Chem. Soc. Rev.*, 1998, **171**, 351; (*b*) T. Ren, C. Lin, P. Amalberti, D. Macikenas, J. D. Protasiewicz, J. C. Baum and T. Gibson, *Inorg. Chem. Commun.*, 1998, **1**, 23.

16 (*a*) V. W. Yam, K. K. Lo, W. K. Fung and C. R. Wang, *Coord. Chem. Rev.*, 1998, **171**, 17; (*b*) H. Kunkely and A. Vogler, *Chem. Commun.*, 1990, 1204.