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Facile synthesis and structures of infinite one-dimensional silver(I) coordination polymers

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Abstract

The synthesis and characterization of the isolated, infinite tubular coordination polymers $\{[Ag(cis\text{-tach})]ClO_4\}_\infty$ (**1**), $\{[Ag(trans\text{-tach})]ClO_4\}_\infty$ (**2**) and $\{[Ag(cis\text{-tach})]BF_4\}_\infty$ (**3**) has been achieved with the isomers *cis,cis*-1,3,5-triaminocyclohexane and *cis,trans*-1,3,5-triaminocyclohexane. Each new material has been fully characterized by single crystal X-ray diffraction, NMR, IR and elemental analysis. Compounds **1**–**3** form definite channels by the trigonal planar coordination of silver(I) metal centres to rigid, aliphatic triamino ligands, forming $4^2 \cdot 6$ topological networks.

Keywords: One-dimensional; Silver(I); Aliphatic amino ligands; Coordination polymers; Tubes; Topology; Supramolecular chemistry; Self assembly; Nanotubes

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes have become of increasing interest due to their uniqueness in size, shape and extraordinary physical properties. Experiments are emerging that investigate the properties of carbon nanotubes, whose structural properties are determined by such features as length, diameter and chirality. Such studies have shown carbon nanotubes to be extremely robust materials, and research into the construction of fibre-composite materials using carbon nanotubes is underway [2]. However, production of single (SWNT) [3–6] and multiple (MWNT) [7] walled carbon nanotubes is both expensive and challenging. Coordination polymers are attractive alternatives as the self-assembly of polynuclear, functional materials provides a flexible and facile route to systems more traditionally formed using a covalent approach [8,9]. This methodology uses coordinative or weaker forces to build-up networks of specific topologies, and has been successful in creating a great number of functional materials that contain channels within a higher dimensionality array [10–13], and a much smaller number that exist as isolated one-dimensional polymers [14–16]. We have recently published the first synthesis of infinite, isolated silver(I) coordination tubes by incorporating a pre-organized, tridentate ligand system that is flexible enough to ‘wrap’ its number of arms to form a tubular network [17].

We herein report the extended synthesis of a variety of silver(I) nanotubes using the isomerically related ligands *cis,cis*-1,3,5-triaminocyclohexane (*cis*-tach) and *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) (Fig. 1). The ligand system in each case has combined rigidity due to the cyclohexane backbone and flexibility due to the primary aliphatic amino groups. The formation of the tubular networks appears to be a function of the nitrogen donor geometry combined with anion effects, and as such comprise a novel synthetic route to the construction of the isolated nanotubes $\{[Ag(cis\text{-tach})]ClO_4\}_\infty$ (**1**), $\{[Ag(trans\text{-tach})]ClO_4\}_\infty$ (**2**) and $\{[Ag(cis\text{-tach})]BF_4\}_\infty$ (**3**).

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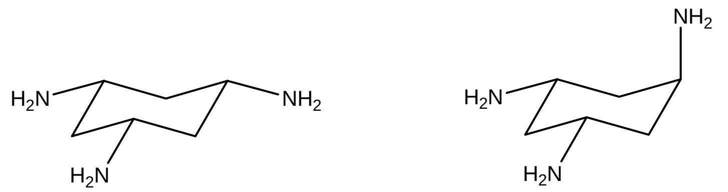

cis,cis-1,3,5-triaminocyclohexane *cis,trans*-1,3,5-triaminocyclohexane

Fig. 1. Ligand geometry facilitating network formation.

2. Experimental

2.1. Materials and physical measurements

Ligands *cis,cis*- and *cis,trans*-1,3,5-triaminocyclohexane were synthesized according to literature methods [18]. All other solvents and reagents were used as purchased without further purification. NMR spectra were measured in D_2O on a Bruker DPX-400 (400 MHz ^1H, 100 MHz ^{13}C). Infrared spectra were obtained from samples prepared as KBr discs in the 650–4000 cm^{-1} range using a Jasco FTIR-410 spectrometer. Elemental analyses were performed on a CE-440 Elemental Analyser.

2.2. Synthesis of compounds **1–3**

2.2.1. Synthesis of [Ag(cis-tach)]ClO$_4$ (**1**)

Silver perchlorate (40 mg, 0.19 mmol) in methanol (3 ml) was added dropwise to a methanolic solution of *cis,cis*-1,3,5-triaminocyclohexane (50 mg, 0.39 mmol) and stirred at room temperature for 1 h, during which white precipitate occurred. Water (5 ml) was added and the mixture stirred for a further 30 min. The resulting cloudy solution was filtered and the clear colourless filtrate yielded colourless needle-like crystals suitable for diffraction by diffusion with ethanol. Yield: 20 mg (0.06 mmol, 32%) $[Ag(C_6H_{15}N_3)]ClO_4$ (334.98); Found (Calc.)%: C 20.99 (21.49), H 4.32 (4.49), N 11.98 (12.48); ^1H NMR (ppm) 0.96 (q, 3H, *J* 11.62 Hz), 2.19 (dt, 3H, *J* 3.83, 11.42 Hz), 3.12 (m, 3H); ^{13}C NMR (ppm) 40.154 (CH_2), 47.124 (CH); FTIR (wavenumbers in cm^{-1}) 3332 (m), 3284 (m), 2919 (w), 2850 (w), 1581 (m), 1457 (w), 1378 (m), 1199 (m), 1074 (s), 1047 (s), 948 (m), 921 (m), 856 (w).

2.2.2. Synthesis of [Ag(trans-tach)]ClO$_4$ (**2**)

Silver perchlorate (53 mg, 0.25 mmol) in methanol (3 ml) was added dropwise to a methanolic solution of *cis,trans*-1,3,5-triaminocyclohexane (65 mg, 0.51 mmol) and stirred at room temperature for 1 h, during which a small amount of white precipitate occurred. The cloudy solution was filtered through a cotton wool plug until clear. The clear colourless filtrate yielded pale brown, block-like crystals suitable for diffraction by slow evaporation over two months. Yield: 41 mg (0.12 mmol, 48%). $[Ag(C_6H_{15}N_3)]ClO_4$; Found (Calc.)%: C 21.38 (21.49), H 4.69 (4.55), N 11.65 (11.72); ^1H NMR (ppm) 1.15 (q, 1H, *J* 11.60 Hz), 1.42 (tt, 2H, *J* 3.93, 12.81 Hz), 1.88 (d, 2H, *J* 13.61 Hz), 2.17 (dt, 1H, *J* 1.80, 11.86 Hz), 3.23 (tt, 2H, *J* 3.83, 11.68 Hz), 3.47 (quin, 1H, *J* 3.41 Hz); ^{13}C NMR (ppm) 37.96 (CH_2), 44.53 (CH_2), 45.19 (CH), 45.73 (CH); FTIR (wavenumbers in cm^{-1}) 3332 (m), 3282 (m), 2904 (w), 2389 (w), 1716 (m), 1579 (m), 1454 (w), 1365 (m), 1351 (m), 1211 (w), 1187 (w), 1068 (s), 993 (s), 970 (s), 875 (m), 844 (m), 806 (m).

2.2.3. Synthesis of [Ag(cis-tach)]BF$_4$ (**3**)

Silver(I) tetrafluoroborate (75 mg, 0.39 mmol) in water (3 ml) was added dropwise to a solution of *cis,cis*-1,3,5-triaminocyclohexane (100 mg, 0.78 mmol) in methanol (2 ml) and the solution stirred for 1 h. The resulting clear, colourless solution was filtered and single crystals suitable for X-ray diffraction were grown by diffusion of ether. Yield: 116 mg (0.358 mmol, 46%). $[Ag(C_6H_{15}N_3)]BF_4$; Found (Calc.)%: C 22.32 (22.25), H 4.65 (4.66), N 12.74 (12.97); ^1H NMR (ppm) 1.03 (q, 3H, *J* 11.60 Hz), 2.17 (dt, 3H, *J* 3.53, 11.34 Hz), 3.15 (tt, 3H, *J* 3.73, 11.05 Hz); ^{13}C NMR (ppm) 39.195 (CH_2), 47.096 (CH); FTIR (wavenumbers in cm^{-1}) 3372 (w), 3347 (m), 3301 (w), 2923 (m), 2852 (m), 2237 (w), 1587 (s), 1459 (s), 1382 (m), 1359 (m), 1290 (w), 1261 (w), 1201 (s), 1074 (s), 948 (m), 923 (m), 856 (w), 806 (m).

2.3. X-ray crystallography

Suitable single crystals of **1**–**3** were prepared and the crystals were mounted on a thin glass fibre using Fomblin oil. X-ray intensity data were measured at 150 K on a Nonius Kappa-CCD diffractometer [λ(Mo Kα) = 0.7107 Å]. Structure solution and refinement for **1**–**3** was carried out with SHELXS-97 [19] and SHELXL-97 [20] via WinGX [21]. Corrections for incident and diffracted beam absorption effects were applied using empirical [22] and numerical methods [23]. None of the crystals showed evidence of crystal decay during data collection. Compounds **1**–**3** crystallized in the space group $P2_1/c$, as determined by systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structures. All structures were solved

Table 1
Crystallographic data for compounds **1**–**3**[a]

	1	**2**	**3**
Empirical formula	$C_6H_{15}AgClN_3O_4$	$C_6H_{15}AgClN_3O_4$	$C_6H_{15}AgBF_4N_3$
Formula weight	336.53	336.53	323.89
Crystal system	monoclinic	monoclinic	monoclinic
a (Å)	8.4778(5)	7.3136(8)	8.4228(4)
b (Å)	7.6947(3)	8.0334(13)	7.6234(4)
c (Å)	16.6640(12)	8.9245(12)	16.4719(8)
α (°)	90	90	90
β (°)	96.803(2)	101.289(8)	97.792(3)
γ (°)	90	90	90
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
V (Å^3)	1079.41(11)	514.20(12)	1047.90(9)
Z value	4	2	4
ρ_{calc} (g/cm^3)	2.071	2.174	2.053
μ (cm^{-1})	2.114	2.219	1.950
T (K)	150(2)	150(2)	150(2)
Number of observations	2121	1559	2061
Residuals: R; R_w	0.0295; 0.0578	0.0590; 0.1041	0.0308; 0.0500

[a] $R_1 = \sum \|\|F_o\| - \|F_c\|\| / \sum \|F_o\|$.
$wR_2 = \left\{ \sum[w(F_o^2 - F_c^2)^2] \middle/ \sum[w(F_o^2)^2] \right\}^{1/2}$.

Table 2
Bond lengths and angles for compounds **1**–**3**

Compound	Bond lengths (Å)		Bond angles (°)	
1	Ag–N(1)	2.403(3)	N(1)–Ag–N(2)	98.15(10)
	Ag–N(2)	2.222(3)	N(1)–Ag–N(3)	111.44(11)
	Ag–N(3)	2.224(3)	N(2)–Ag–N(3)	150.28(11)
2	Ag–N(1)	2.273(11)	N(1)–Ag–N(2)	133.5(4)
	Ag–N(2)	2.276(10)	N(1)–Ag–N(3)	108.4(4)
	Ag–N(3)	2.345(11)	N(2)–Ag–N(3)	118.1(4)
3	Ag–N(1)	2.227(3)	N(1)–Ag–N(2)	150.33(11)
	Ag–N(2)	2.227(3)	N(1)–Ag–N(3)	111.71(11)
	Ag–N(3)	2.391(3)	N(2)–Ag–N(3)	97.89(10)

by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters and refinement statistics for **1**–**3** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1**–**3** are given in Table 2.

3. Results and discussion

3.1. Structural analysis of compounds *1*–*3*

Crystallization of a methanolic mixture of *cis,cis*-1,3,5-triaminocyclohexane with $AgClO_4$ and $AgBF_4$ and *cis,trans*-1,3,5-triaminocyclohexane with $AgClO_4$ results in the formation of infinite one-dimensional coordination polymers. Each structure contains a metal to ligand ratio of 1:1 and the asymmetric unit in each case consists of one ligand, one silver(I) ion and one counter ion. None of the structures presented here contain solvent molecules (see Fig. 2).

Both the trigonal planar silver(I) ions and the tridentate amino ligands can be seen as three-coordinate units, which self-assemble to form $4^2 \cdot 6$ topological networks. The macrocycles formed upon coordination facilitate a tubular structure with a definite channel. The channels found in compounds **1**, **2** and **3** are not large enough to encapsulate a further molecule, having dimensions of 5.4, 5.3 and 5.6 Å, respectively. The isolated one-dimensional polymers together form an extensive three-dimensional hydrogen-bonded network linked via interactions between the coordinating amino groups and the counter ions (Fig. 3).

The manner in which these rigid ligands facilitate the formation of tubular networks is dependent upon their coordination geometry. The molecule *cis*-tach is a tripodal ligand, where the three equatorial amino residues can wrap around the walls of the channel (Fig. 4(a)). *trans*-Tach, on the other hand, has the ability to coordinate in a linear polymer via the two equatorial groups along a chain (Fig. 4(b)), and further coordination via the axial amino group connects to a silver(I) centre of a second chain and forms the tubular structure (Fig. 4(c)). The macrocyles formed in each case by two silver(I) ions and two ligands consist of 12 atoms and have an inversion centre.

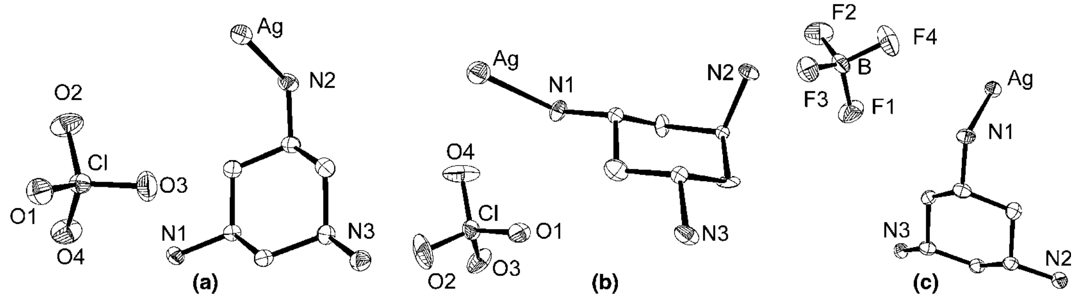

Fig. 2. Asymmetric unit of **1 (a)**, **2 (b)** and **3 (c)**. Note the coordination environment of the silver ion lies between T-shaped planar and trigonal planar, with the Ag ion being ligated to three amino groups of different tach ligands.

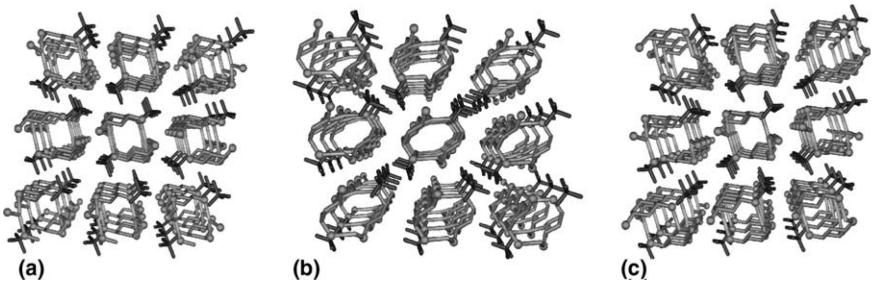

Fig. 3. Three-dimensional hydrogen bonded networks of (a) compound **1**, (b) compound **2** and (c) compound **3** showing isolated coordination polymers. The anions are shown by the black tetrahedra and the nitrogen atoms of the tach-based ligands are shown as spheres.

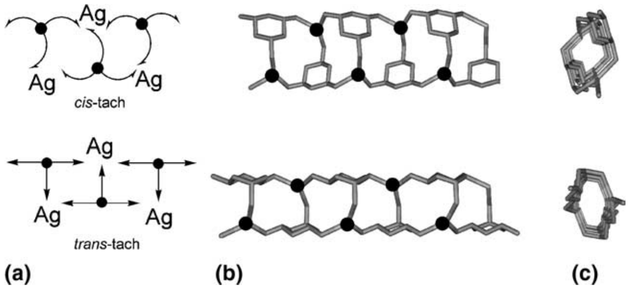

Fig. 4. (a) Ligand motifs of *cis*- and *trans*-tach shown as black dots with arrows. (b) Macrocycle formation utilizing the different ligand geometries with the silver ions show as black dots. (c) End-on view of tubes showing channels.

3.2. Conclusions

We have investigated the synthesis of a number of infinite one-dimensional coordination polymers of aliphatic triamino ligands with a variety of silver(I) salts in order to determine whether such ligand systems can be used as building blocks in the rational design of new functional materials. The isomeric ligands *cis,cis*-1,3,5-triaminocyclohexane and *cis,trans*-1,3,5-triaminocyclohexane have aliphatic amino groups, the direction of which have been proven to provide valuable freedom in the self-assembly process. The construction of these infinite tubular polymers from metal–ligand systems that posses a degree of pre-organization and a number of arms that can 'wrap' can be seen as a noteworthy development in the self-assembly of nanotubular compounds. We are currently extending this work by investigation into the coordination of our rigid amines with other metals and also via derivatization of the amino residues in order to enlarge the channel dimensions and increase the functionality of the materials.

4. Supplementary material

Crystallographic data (X-ray data in *.cif files) for structures **1**–**3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 233831 for compound **1**, CCDC No. 233832 for compound **2** and CCDC No. 233833 for compound **3**. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] S. Iijima, Nature 56 (1991) 354.
[2] A.A. Mamedov, N.A. Kotov, M. Prato, D.M. Guldi, J.P. Wicksted, A. Hirsch, Nature Mater. 1 (2002) 190.
[3] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.
[4] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605.
[5] P.M. Ajayan, J.M. Lambert, P. Bernier, L. Barbedette, C. Colliex, J.M. Planeix, Chem. Phys. Lett. 215 (1993) 509.
[6] T. Guo, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. 243 (1995) 49.
[7] T.W. Ebbesen, P.M. Ajayan, Nature 358 (1992) 220.
[8] H. Liu, S. Xiao, H. Gan, T. Jiu, H. Li, L. Jiang, D. Zhu, D. Yu, B. Xiang, Y. Chen, J. Am. Chem. Soc. 125 (2003) 10794.
[9] J. Liu, M. Shao, X. Chen, W. Yu, X. Liu, Y. Qian, J. Am. Chem. Soc. 125 (2003) 8088.
[10] M.J. Zaworotko, Angew. Chem. Int. Ed. 39 (2000) 3052.
[11] Y. Cui, J. Lee, W. Lin, J. Am. Chem. Soc. 125 (2003) 6014.
[12] P. Jenson, S.R. Batten, B. Moubaraki, K.S. Murray, J. Chem. Soc., Dalton Trans. (2002) 3712.
[13] M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou, A.S.C. Chan, Angew. Chem. Int. Ed. 39 (2000) 2468.
[14] M. Aoyagi, S. Tashiro, M. Tominaga, K. Biradha, M. Fujita, Chem. Commun. (2002) 2036.
[15] J. Fan, H.-F. Zhu, T.-A. Okamura, W.-Y. Sun, W.-X. Tang, N. Ueyama, Inorg. Chem. 42 (2003) 158.
[16] Y. Kang, S.S. Lee, K.-M. Park, S.H. Lee, S.O. Kang, J. Ko, Inorg. Chem. 40 (2001) 7027.
[17] A.L. Pickering, G. Seeber, D.-L. Long, L. Cronin, Chem. Commun. (2004) 136.
[18] F. Lions, K.V. Martin, J. Am. Chem. Soc. 79 (1957) 15721.
[19] G.M. Sheldrick, Acta Crystallogr., Section A A46 (1998) 467.

[20] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Analysis, University of Göttingen, Germany, 1997.

[21] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.

[22] R.H. Blessing, Acta Crystallogr., Section A 51 (1995) 33.

[23] P. Coppens, L. Leiserowitz, D. Rabinovich, Acta Crystallogr. 18 (1965) 1035.