A novel $(CF_3SO_3^-)_6$ cluster with multiple F···F interactions: crystal structure of a self-assembled trinuclear Ag(I) complex with the tripodal ligand tris(2-benzimidazolylmethyl)amine

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Self-assembly of silver(I) trifluoromethanesulfonate with the tripodal ligand tris(2-benzimidazolylmethyl)amine (ntb) affords the trinuclear complex $[Ag_3(ntb)_2](CF_3SO_3)_3$, which exhibits a rhombohedral network formed from N–H···O hydrogen bonds and weak Ag···O interactions linking $[Ag_3(ntb)_2]^{3+}$ cations with a novel S_6-symmetric $(CF_3SO_3^-)_6$ cluster consolidated by multiple F···F interactions.

The controlled design of solid-state architectures has become a rapidly developing area of current research.[1] Much effort has been devoted to the investigation of supramolecular contacts that are responsible for the construction of multi-dimensional frameworks, and strategies based on the concept of *supramolecular synthons*[2a,b] have proved to be fruitful in crystal engineering.[2] A variety of weak intermolecular interactions[2c,d] such as halogen···halogen, N···halogen, S···S, π···π stacking, M···M, O–H···M, M–H···O, C–H···M and various types of weak hydrogen bonds (C–H···O, C–H···N, O–H···π, C–H···π), in contrast to the traditional hydrogen bonds (X–H···Y; X, Y = F, O and N), have been recognized in the generation of supramolecular synthons.

As a sequel to our studies on metal complexes with tripodal ligands,[3] we have synthesized a series of mononuclear to tetranuclear silver(I) complexes of tris(*N*-R-benzimidazol-2-yl-methyl)amine, $[Ag(Prntb)(CF_3SO_3)]\cdot0.25H_2O$ (R = *n*-Pr) **1**, $[Ag_2(Mentb)_2](CF_3SO_3)\cdot H_2O$ (R = Me) **2**, $[Ag_3(Etntb)_2](ClO_4)\cdot CH_3OH$ (R = Et) **3** and $[Ag_4(ntb)_2(CH_3CN)_2(CF_3SO_3)_2](CF_3-CO_2)_2\cdot2H_2O$ (R = H) **4** in which various kinds of weak intermolecular interactions play important roles in the crystal packing.[4] This paper reports a new complex $[Ag_3(ntb)_2]-(CF_3SO_3)_3$ **5** formed by supramolecular linkage of the triuclear cations with a novel hexameric cluster $(CF_3SO_3^-)_6$ that is held together by multiple intermolecular F···F contacts.

Complex **5** was prepared by the reaction of $AgCF_3SO_3$ with ntb in a molar ratio of 3:2 in MeOH/DMF.† Elemental analyses indicated the formulation $Ag_3(ntb)_2(CF_3SO_3)_3$, and single-crystal X-ray analysis‡ revealed **5** to have a three-dimensional network $\{2[Ag_3(ntb)_2]^{3+}(CF_3SO_3^-)_6\}_\infty$ stabilized by N–H···O hydrogen bonds and weak Ag···O interactions.

It is well known that the d^{10} silver(I) ion exhibits flexible coordination environments ranging from linear to octahedral.[5] In the crystal structure of **5**, each Ag(I) ion is linearly coordinated by two imidazole nitrogen atoms belonging to two ntb ligands, and three triangularly arranged Ag(I) ions thus assemble two tripodal tridentate ligands to form a sandwich structure of symmetry C_3 (Fig. 1), which closely resembles that in **3**. The intermetallic distances of 3.4452(5) Å in $[Ag_3(ntb)_2]^{3+}$ is comparable to that (3.439(1) Å) in the $Ag_6(im)_{12}$ cluster,[6] but significantly longer than the corresponding distance of 3.107(1) Å in **3**.[4]

The most notable structural feature of **5** is the occurrence of a novel supramolecular $(CF_3SO_3^-)_6$ cluster that is held together
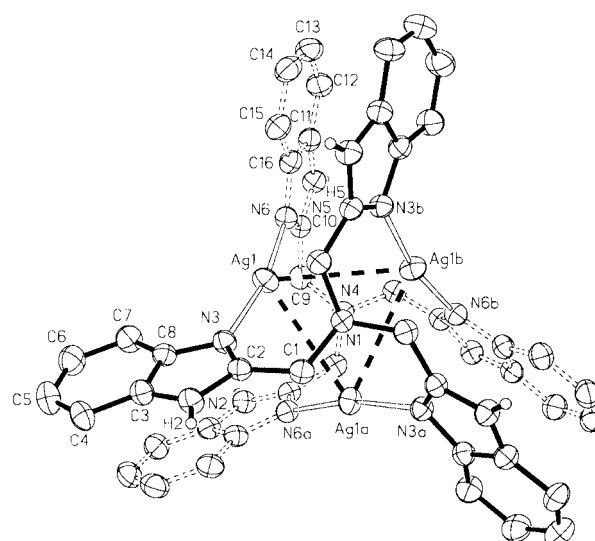
**Fig. 1** Perspective view of the $[Ag_3(ntb)_2]^{3+}$ cation of symmetry 3 (C_3) showing atoms as thermal ellipsoids at the 30% probability level. All H atoms have been omitted, except those of the NH groups that are shown as small spheres.

(a)   (b)
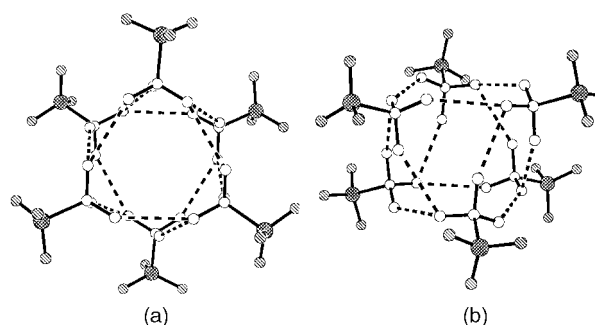
Fig. 2 The $(CF_3SO_3^-)_6$ cluster viewed (a) along the $\bar{3}$ (S_6) symmetry axis showing six triflate anions held together by twelve F···F interactions (represented by broken lines) and (b) from the side with the $\bar{3}$ axis aligned vertically.

by twelve F···F interactions. The well-ordered trifluoromethanesulfonate (triflate) anion is not involved in coordination to Ag(I). As shown in Fig. 2, six symmetry-related $CF_3SO_3^-$ anions have their F atoms clustering about a crystallographic $\bar{3}$ (S_6) center. Two F_{eq} (equatorial fluorine) atoms in each anion have approximately the same z coordinate as the S atom, so that three anions related by the threefold axis are alternately connected by three $F_{eq}\cdots F_{eq}$ contacts of 2.788(7) Å to form a nine-membered, puckered $(F_{eq}-C-F_{eq}\cdots)_3$ ring, with three F_{ax} (axial fluorine) atoms pointing toward the inversion-related
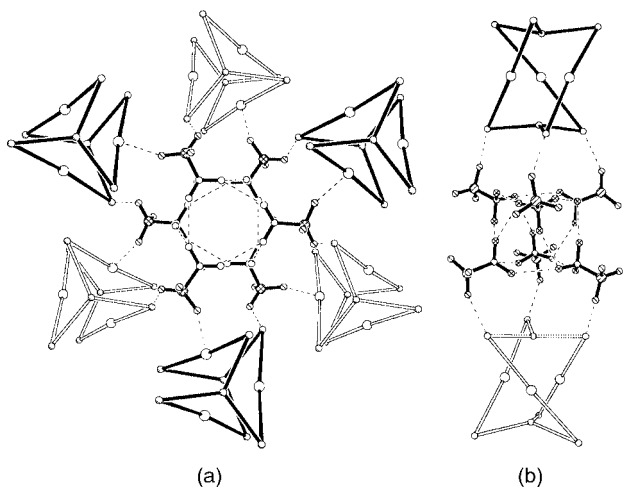
Fig. 3 (a) Concavo-concave layer constructed from N–H⋯O hydrogen bonds and Ag⋯O interactions, matching the (001) plane. For clarity, the 2-benzimidazolylmethyl arms of the ntb ligand are represented by long solid and open rods for $[Ag_3(ntb)_2]^{3+}$ cations lying above and below, respectively, the level of the central $(CF_3SO_3^-)_6$ cluster, each joining an NH group to the silver(I) ion and the tertiary nitrogen atom. (b) Side-on view showing the linkage of the cluster to a pair of cations in adjacent layers by additional N–H⋯O hydrogen bonds. All weak interactions are represented by broken lines.

nine-membered ring; further inter-ring $F_{ax}⋯F_{eq}$ interactions of length 2.822(5) Å then generate the $(CF_3SO_3^-)_6$ cluster.

The hexameric cluster controls the packing of the $[Ag_3(ntb)_2]^{3+}$ cations through intermolecular interactions involving its six abducent SO_3^- groups (SO_3^- groups that extend outward from the hexameric cluster). One oxygen atom of each sulfonate group interacts weakly with the silver(I) atom at Ag⋯O 3.074(4) Å, which is too long for covalent bonding but may be considered as a non-bonded electrostatic interaction.[7] The other two oxygen atoms interact with the NH groups of two different $[Ag_3(ntb)_2]^{3+}$ cations, forming an "in-plane" N–H⋯O hydrogen bond (N⋯O 2.819(4) Å) which, together with the Ag⋯O interactions, generate a concavo-concave layer matching the (001) plane, as shown in Fig. 3(a), and an "out-of-plane" type (N⋯O 2.762(4) Å) for connecting adjacent layers as depicted in Fig. 3(b). Thus the S_6-symmetric $(CF_3SO_3^-)_6$ cluster can be regarded as a novel cooperative supramolecular synthon mediated by multiple F⋯F interactions, being connected to the $[Ag_3(ntb)_2]^{3+}$ cations by N–H⋯O hydrogen bonds and weak non-bonded Ag⋯O interactions to generate a three-dimensional network. There exist intramolecular offset π⋯π interactions (3.2 Å) between three pairs of benzimidazole rings of two ntb ligands in the complex, but no significant intermolecular π⋯π interaction is found, suggesting that the mode of molecular packing is dominated by the $(CF_3SO_3^-)_6$ supramolecular synthon. From an alternative point of view, every $(CF_3SO_3^-)_6$ cluster interacts with eight $[Ag_3(ntb)_2]^{3+}$ cations, and the extended molecular assembly of **5** can be visualized as a network of β-polonium structural type[8] with $[Ag_3(ntb)_2]^{3+}$ cations at the nodes and virtual lines between the cations as connections, in which half of the large cavities (*ca*. 12 × 13 × 13 Å³) are occupied by hexameric clusters (see Fig. 4) while the other half are entirely empty.

The "chloro-rule" has been known for a long time in organic crystal chemistry,[9] and specific, attractive intramolecular halogen⋯halogen interactions, X⋯X (X = Cl, Br or I) are well established in molecular crystal engineering.[10] For example, in crystalline tetrakis(4-bromophenyl)methane a diamondoid network is formed by linking the tetraphenylmethane units with the tetrahedral Br₄ supramolecular synthon in which the Br⋯Br distance is 3.91 Å.[10a] However, the nature of X⋯X is still a matter of debate,[10] and so far the F⋯F interaction has attracted little attention. Nevertheless, a survey of the Cambridge Structural Database revealed a number of F⋯F contacts within the range of 2.50 to 2.85 Å for triflate-
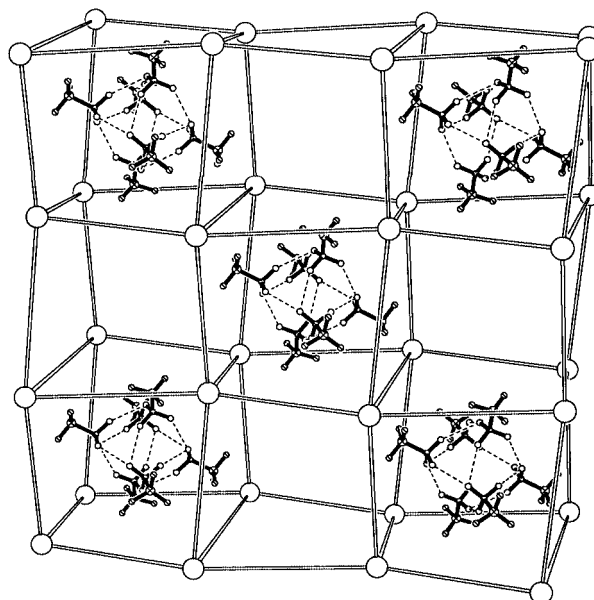
Fig. 4 Schematic representation of the β-polonium-type network of **5**, with large spheres representing $[Ag_3(ntb)_2]^{3+}$ cations located at the nodes and $(CF_3SO_3^-)_6$ clusters occupying half of the cages. Note the long open rods merely outline the network topology and do not indicate intermolecular interactions.

containing structures, exclusive of those involving disordered triflate groups, indicating that F⋯F interactions are prevalent in many crystal structures. In this connection it is noted that Kowalik *et al.* recently reported the crystal structure of 6-perfluorohexylsulfonyl-2-naphthol that exhibits attractive non-bonded F⋯F interactions of 2.85 Å.[11] To our knowledge the present study provides the first example of a $(CF_3SO_3^-)_6$ cluster consolidated by multiple intermolecular F⋯F interactions. Assembly of the hexameric cluster is facilitated by charge delocalization of its component triflate anions over all O and F atoms. Furthermore, the mode of molecular packing in **5** is attributable to the precise synergistic effect of multiple F⋯F interactions with N–H⋯O hydrogen bonds and weak Ag⋯O interactions.

Acknowledgements

Notes and references

† Preparation: $AgCF_3SO_3$ (0.077 g, 0.3 mmol) dissolved in methanol (50 cm³) was added to a solution of ntb (0.081 g, 0.2 mmol) in methanol (50 cm³). The white precipitate that appeared immediately was dissolved in DMF and the resulting mixture was left standing for several days to afford colorless crystals of **5**. Found: C, 38.78; H, 2.81; N, 12.08. Calc. for $C_{51}H_{42}F_9N_{14}O_9S_3Ag_3$: C, 38.63; H, 2.67; N, 12.36%. ¹H NMR (DMSO-d_6): δ 12.92 (s, 1 H, NH), 7.38, 7.26, 7.12, 7.00 (s, 4 H, aromatic H), 4.24 (s, 2 H, CH₂). FAB-MS: *m/z* 514 $[Ag(ntb)]^+$. IR (KBr, cm⁻¹): 1625, 1596 [ν(C=N)], 1264 [ν(O–S)]. UV/vis (CH₃CN, λ/nm): 281, 274, 243 and 209.

‡ Crystal data for **5**: $C_{51}H_{42}F_9N_{14}O_9S_3Ag_3$, $M = 1585.8$, rhombohedral, space group $R\bar{3}$ (no. 148), $a = 15.758(1)$, $c = 40.459(4)$ Å, $U = 8700.6(12)$ Å³, $Z = 6$, $T = 293$ K, crystal size $0.1 × 0.2 × 0.2$ mm³, 9159 reflections measured, final $R1 = 0.0509$ and $wR2 = 0.1523$ for 3238 observed $[I > 2\sigma(I)]$ reflections. CCDC reference number 186/1958. See http://www.rsc.org/suppdata/dt/b0/b002411m/ for crystallographic files in .cif format.

1 (*a*) M. J. Hannon, C. L. Painting and W. Errington, *Chem Commun.*, 1997, 1805; (*b*) G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature* (*London*), 1995, **374**, 792; (*c*) S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8720; (*d*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2638.

2 (*a*) G. R. Desiraju, *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2311; (*b*) G. R. Desiraju, *Chem. Commun.*, 1997, 1475; (*c*) *The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, Wiley, Chichester, 1996; (*d*) A. Nangia and G. R. Desiraju, in *Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets*, ed. J. Veciana, C. Rovira and D. B. Amabilino, Kluwer, Dordrecht, 1999, pp. 1–21.

3 (*a*) C.-Y. Su, B.-S. Kang, H.-Q. Liu, Q.-G. Wang and T. C. W. Mak, *Chem. Commun.*, 1998, 1551; (*b*) C.-Y. Su, B.-S. Kang, T.-B. Wen, Y.-X. Tong, X.-P. Yang, C. Zhang, H.-Q. Liu and J. Sun, *Polyhedron*, 1999, **18**, 1577; (*c*) C.-Y. Su, B.-S. Kang, X.-Q. Mu, J. Sun, Y.-X. Tong and Z.-N. Chen, *Aust. J. Chem.*, 1998, **51**, 561; (*d*) C.-Y. Su, Q. Zhou, W.-J. Zhang, Z.-L. Lu and B.-S. Kang, *Chem. Res. Chin. Univ.*, 1999, **15**, 63.

4 C.-Y. Su, B.-S. Kang, Q.-C. Yang and T. C. W. Mak, *Inorg. Chem.*, to be published.

5 (*a*) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 6th edn., 1999, p. 1085; (*b*) C. V. K. Sharma and R. D. Rogers, *Cryst. Eng.*, 1998, **1**, 19.

6 G. W. Eastland, M. A. Mazid, D. R. Russell and M. C. R. Symons, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 1682.

7 C.-M. Che, H.-K. Yip, D. Li, S.-M. Peng, G.-H. Lee, Y.-M. Wang and S.-T. Liu, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1615.

8 T. C. W. Mak and B. R. F. Bracke in ref 2(*d*), ch. 2, pp. 24–25.

9 (*a*) G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647; (*b*) J. A. R. P. Sarma and G. R. Desiraju, *Acc. Chem. Res.*, 1986, **19**, 222.

10 (*a*) D. S. Reddy, D. C. Craig and G. R. Desiraju, *J. Am. Chem. Soc.*, 1996, **118**, 4090; (*b*) V. R. Pedireddi, D. S. Reddy, B. S. Goud, D. C. Craig, A. D. Rae and G. R. Desiraju, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 2353; (*c*) S. L. Price, A. J. Stone, J. Lucas, R. S. Rowland and A. E. Thornley, *J. Am. Chem. Soc.*, 1994, **116**, 4910; (*d*) R. Thaimattam, D. S. Reddy, F. Xue, T. C. W. Mak, A. Nangia and G. R. Desiraju, *New J. Chem.*, 1998, **22**, 143.

11 J. Kowalik, D. VanDerveer, C. Clower and L. M. Tolbert, *Chem. Commun.*, 1999, 2007.