Formation of Mono-, Bi-, Tri-, and Tetranuclear Ag(I) Complexes of C_3-Symmetric Tripodal Benzimidazole Ligands

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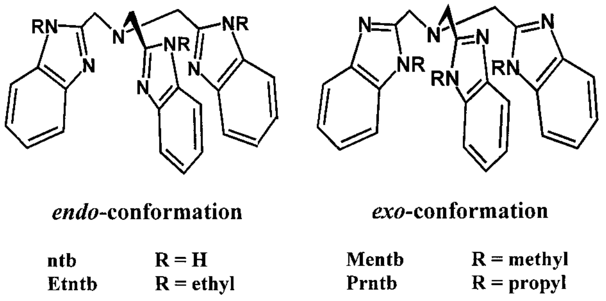
The C_3-symmetric tripodal ligand tris(2-benzimidazolylmethyl)amine (ntb) and its alkyl-substituted derivatives tris(*N*-R-benzimidazol-2-ylmethyl)amine (R = methyl, Mentb; R = ethyl, Etntb; R = propyl, Prntb) react with various silver(I) salts to afford mononuclear $[Ag(Prntb)(CF_3SO_3)]\cdot 0.25H_2O$, **1**, binuclear $[Ag_2(Mentb)_2](CF_3SO_3)_2\cdot H_2O$, **2**, trinuclear $[Ag_3(Etntb)_2](ClO_4)_3\cdot CH_3OH$, **3**, and tetranuclear $[Ag_4(ntb)_2(CH_3CN)_2(CF_3CO_2)_2](CF_3CO_2)_2\cdot 2H_2O$, **4**. All four complexes have been characterized by elemental analyses, IR spectroscopy, and X-ray crystallography. The Ag(I) ion in **1** is coordinated to the three imine nitrogen atoms of the Prntb ligand and one oxygen atom of the trifluoromethanesulfonate anion in a distorted tetrahedral environment. Dinuclear **2** has C_2 symmetry with each Ag(I) atom trigonally coordinated by two arms of one Mentb and one arm of another. Trinuclear **3** has C_3 symmetry with a Ag_3 regular triangle sandwiched between a pair of Etntb ligands such that one arm of each ligand is involved in linear coordination about an Ag(I) atom. In the tetranuclear complex **4**, two linearly coordinated Ag(I) atoms lying on the molecular C_2 axis are bridged by a pair of ntb ligands and the remaining pendant arm of each ntb ligand is attached to another Ag(I) atom whose tetrahedral coordination sphere is completed by an acetonitrile molecule and a chelating trifluoroacetate anion. Complexes **2** and **3** may be regarded as an aggregation of two tridentate ligands by a silver dimer and a trinuclear cluster with weak $Ag\cdots Ag$ interactions, respectively, while in **4** the aggregation of two tripodal ligands by four Ag(I) ions affords a multicomponent internal cavity. The packing modes of complexes **1**−**3** are dominated by weak supramolecular $\pi\cdots\pi$ and $CH\cdots\pi$ interactions. Hexagonal or square channels are generated in **1** and **2,** and a honeycomb layer structure is formed in **3** with solvate molecules and counteranions occupying the voids. The crystal structure of **4** consists of a three-dimensional network consolidated by $NH\cdots O$ and $OH\cdots O$ hydrogen bonds.

Introduction

Tripodal ligands have long been used in both coordination and organometallic chemistry,[1] typically polypyrazolylborate and tris(2-pyridyl) tripodal ligands. However, their potential use in supramolecular chemistry for the construction of various cage-like or boxlike complexes has not been fully realized until quite recently.[2] In particular, the use of C_3-symmetric tripodal ligands in crystal engineering has been reviewed.[3] In our studies of the metal complexes of polybenzimidazole tripodal ligands,[4] it was found that tris(2-benzimidazolylmethyl)amine (ntb) and its alkyl-substituted derivatives tris(*N*-R-benzimidazol-2-ylmethyl)amine (Rntb) (see Chart 1) possess cavities of an appropriate size to encapsulate a lanthanide(III) ion, giving complexes with either a 1:1[4a] or a 1:2[4b] metal-to-ligand ratio. Furthermore, construction

Chart 1



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of two- or three-dimensional supramolecular networks with the encapsulated lanthanide(III) complexes as building blocks has also been realized.[5] Since the three arms of this type of ligand can each rotate freely around an $N_{apical}-C$ bond, multicomponent compounds or coordination polymeric networks may be expected to form from the assembly of these ligands by metal ions of low coordination number. As silver(I) is known to exhibit flexible coordination geometries (linear, bent, trigonal planar, T-shaped, tetrahedral, trigonal pyramidal, etc.) in its complexes with polydentate ligands,[1,6] we have systematically synthesized mono- to tetranuclear silver(I) complexes of selected C_3-symmetric tripodal ligands in an effort to understand the coordination behavior of such ligands, as well as the factors influencing their crystal packing modes.

Experimental Section

Materials. Silver perchlorate hydrate ($AgClO_4 \cdot xH_2O$, Aldrich), silver trifluoroacetate (CF_3CO_2Ag, Aldrich), silver trifluoromethanesulfonate (triflate, CF_3SO_3Ag, Aldrich), potassium (K, Merck), nitrilotriacetic acid ($C_6H_9NO_6$, ACROS), 1,2-phenylenediamine ($C_6H_8N_2$, Riedel-de Haën), iodomethane (CH_3I, ACROS), iodoethane (C_2H_5I, ACROS), 1-iodopropane (C_3H_7I, ACROS), methanol (CH_3OH, Lab-Scan), acetonitrile (CH_3CN, Lab-Scan), tetrahydrofuran (THF, C_4H_8O, Lab-Scan), diethyl ether ($C_4H_{10}O$, Scharlau), and diethylene glycol ($C_4H_{10}O_3$, Lab-Scan) were used as purchased without further purification.

Physical Measurements. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer Paragon 500 FT-IR spectrometer using KBr disks. ^1H NMR spectra were measured on a Bruker DOX 300 instrument using DMSO-d_6 as solvent and TMS as an internal standard at room temperature.

Preparations. All chemicals and solvents used for the synthesis were reagent grade.

Caution: Perchlorate salt is potentially explosive and should only be handled in small quantities, although we worked with it without any incident.

The ligand tris(2-benzimidazolylmethyl)amine (ntb) was synthesized following a slight modification of the literature method[7] using diethylene glycol as the reaction media. The ligands tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) and tris(*N*-ethylbenzimidazol-2-ylmethyl)amine (Etntb) were prepared according to the reported procedure.[8] These three compounds are identified by IR and H^1 NMR spectra as follows.

Ntb. IR (KBr, cm^{-1}): 3122br, 2923w, 1623m, 1591m, 1535m, 1443s, 1350m, 1273s, 1216m, 1124m, 1025s, 968m, 840m, 742s, 479w, 437w. ^1H NMR (DMSO-d_6): δ 12.2 (3 H, broad, N*H*), 7.61 (6 H, dd, *H*2, *H*5), 7.22 (6 H, dd, *H*3, *H*4), 4.08 (6 H, s, *H*1).

Mentb. IR (KBr, cm^{-1}): 3055w, 2937w, 1675w, 1613m, 1509m, 1474s, 1440s, 1398s, 1329s, 1287m, 1239m, 1148m, 1100s, 996m, 864m, 746s, 448w. ^1H NMR (DMSO-d_6): δ 7.66 (3 H, dd, *H*2), 7.24 (3 H, dd, *H*5), 7.22 (6 H, dd, *H*3, *H*4), 4.22(6 H, s, *H*1), 3.45 (9 H, s, $-CH_3$).

Etntb. IR (KBr, cm^{-1}): 3056w, 2973w, 1655m, 1613m, 1509m, 1460s, 1419s, 1363m, 1336s, 1280m, 1232m, 1162m, 1093s, 982m, 857m, 746s, 413w. ^1H NMR (DMSO-d_6): δ 7.66 (3 H, dd, *H*2), 7.35 (3 H, dd, *H*5), 7.21 (6 H, dd, *H*3, *H*4), 4.25(6 H, s, *H*1), 4.60 (6 H, q, $-CH_2-$), 0.75 (9 H, t, $-CH_3$).

Tris(*N*-propylbenzimidazol-2-ylmethyl)amine (Prntb). Metallic potassium (1.17 g, 0.03 mol) was added carefully in small portions to a suspension of ntb (4.07 g, 0.01 mol) in 100 mL of dry THF under nitrogen atmosphere with vigorous stirring. After H_2 ceased to bubble, the solution was heated gently to reflux for 2 h. 1-Iodopropane (5.1 g, 0.03 mol) was added dropwise within 10 min, and the mixture was refluxed further for 3 h. The solvent was removed under reduced pressure, and the resulting white precipitate was recrystallized from methanol/water to give 2.4 g of Prntb. Yield: 46%. Anal. Calcd for $C_{33}H_{33}N_7$: C, 75.11; H, 6.30; N, 18.59. Found: C, 74.83; H, 6.51; N, 18.32. IR (KBr, cm^{-1}): 3051w, 2966w, 1653m, 1611m, 1513m, 1464s, 1415s, 1366m, 1331m, 1288m, 1253m, 1169m, 1092s, 993m, 853m, 733s, 410w. ^1H NMR (DMSO-d_6): δ 7.65 (3 H, dd, *H*2), 7.40 (3 H, dd, *H*5), 7.20 (6 H, dd, *H*3, *H*4), 4.17(6 H, s, *H*1), 4.48 (6 H, t, $-CH_2CH_2CH_3$), 1.15 (6 H, m, $-CH_2CH_2CH_3$), 0.18 (9 H, t, $-CH_3$).

$[Ag(Prntb)(CF_3SO_3)] \cdot 0.25H_2O$, 1. To a solution of Prntb (53 mg, 0.1 mmol) in 5 mL of methanol was added a solution of $AgCF_3SO_3$ (26 mg, 0.1 mmol) in 5 mL of acetonitrile. The resulting clear mixture was stored in a test tube, which was placed in a large stoppered flask containing diethyl ether to allow vapor diffusion of diethyl ether into the mixture. After several days a colorless blocklike crystalline product appeared and was collected. Yield: 54%. Anal. Calcd for $C_{34}H_{39.5}N_7O_{3.25}F_3SAg$: C, 51.36; H, 5.00; N, 12.33. Found: C, 51.85; H, 5.17; N, 12.14. IR (KBr, cm^{-1}): 3493br, 3051w, 2966w, 1618m, 1471s, 1352m, 1331m, 1281s, 1253s, 1155s, 1029s, 895w, 867w, 748s, 636s, 572m, 516m, 418w.

$[Ag_2(Mentb)_2](CF_3SO_3)_2 \cdot H_2O$, 2. The ligand Mentb (45 mg, 0.1 mmol) was dissolved in 5 mL of hot methanol, and a solution of $AgCF_3SO_3$ (26 mg, 0.1 mmol) in 5 mL of acetonitrile was added slowly. The resulting mixture was left standing for several days to precipitate a colorless crystalline solid. The product was collected, washed with methanol and diethyl ether, and dried in air. Yield: 78%. Anal. Calcd for $C_{56}H_{56}N_{14}O_7F_6S_2Ag_2$: C, 47.60; H, 3.85; N, 13.88. Found: C, 47.68; H, 4.01; N, 13.69. IR (KBr, cm^{-1}): 3464br, 3057w, 2946w, 1609m, 1483s, 1450m, 1362m, 1332m, 1261s, 1162s, 1105m, 1028s, 902w, 860w, 748s, 636s, 573m, 517m, 447w.

$[Ag_3(Etntb)_2](ClO_4)_3 \cdot CH_3OH$, 3. To a solution of Etntb (49 mg, 0.1 mmol) in 5 mL of methanol was added a solution of $AgClO_4 \cdot xH_2O$ (31 mg, 0.15 mmol) in 5 mL of acetonitrile. Colorless crystals precipitated after slow evaporation of the solvent for several days in air. Yield: 56%. Anal. Calcd for $C_{61}H_{70}N_{14}Cl_3O_{13}Ag_3$: C, 44.75; H, 4.31; N, 11.98. Found: C, 44.55; H, 4.16; N, 12.57. IR (KBr, cm^{-1}): 3484br, 3044w, 2981w, 1616m, 1490s, 1448s, 1378m, 1336m, 1266w, 1231w, 1091s, 1007m, 902w, 860w, 741s, 622s, 524w, 426w.

$[Ag_4(ntb)_2(CF_3CO_2)_2(CH_3CN)_2](CF_3CO_2)_2 \cdot 2H_2O$, 4. The ligand ntb (82 mg, 0.2 mmol) was dissolved in 10 mL of hot methanol, and a solution of $AgCF_3CO_2$ (88 mg, 0.4 mmol) in 5 mL of acetonitrile was added slowly. The resulting mixture was left standing for several days to allow the solvent to evaporate slowly. The colorless precipitate was collected and dried in air. Yield: 37%. Anal. Calcd for $C_{60}H_{52}N_{16}O_{10}F_{12}Ag_4$: C, 39.67; H, 2.89; N, 12.34. Found: C, 39.75; H, 3.21; N, 11.98. IR (KBr, cm^{-1}): 3430br, 3064w, 2924w, 2334w, 1668s, 1541w, 1457m, 1450m, 1351w, 1316w, 1281m, 1204s, 1134s, 1028w, 972w, 839m, 797m, 741m, 670w, 516w, 438w.

X-ray Data Collection, Structure Solution, and Refinement. Data collection for **1** was performed at 293 K on a Siemens P4/PC four-circle diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), using the $\omega-2\theta$ scan technique to a maximum 2θ value of 52°. The cell parameters were determined by a least-squares fit to 35 carefully centered reflections in the range $9.81 < 2\theta < 24.86°$. Of the 8542 reflections collected, 7319 were unique ($R_{int} = 0.0397$). The intensities of three representative reflections were measured after every 200 reflections. An empirical absorption correction based on ψ scans of several reflections was applied, which resulted in transmission factors ranging from 0.86 to 0.89. The data were corrected for Lorentz and polarization effects. The intensities for **2**−**4** were collected on a MSC/Rigaku RAXIS IIC image-plate diffractometer at 293 K using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) from a rotating-anode X-ray generator operating at 50 kV and 90 mA. For **2**, 36 oscillation photographs were taken with a total oscillation range of 0−180°, oscillation angle of 6°, and exposure time of 8 min/frame. For **3**, they were taken with 60 oscillation frames in the range 0−180° with an oscillation angle of 3° and an time exposure of 8 min/frame, and for **4**, they were taken with 55 oscillation frames in the range 0−180° with an oscillation angle of 3° and an exposure time of 8 min/

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Table 1. Crystallographic Data for Complexes **1**−**4**

	1	**2**	**3**	**4**
formula	$C_{34}H_{39.5}F_3N_7O_{3.25}SAg$	$C_{56}H_{56}F_6N_{14}O_7S_2Ag_2$	$C_{61}H_{70}N_{14}Cl_3O_{13}Ag_3$	$C_{60}H_{52}F_{12}N_{16}O_{10}Ag_4$
fw	795.16	1431.01	1637.27	1816.66
cryst syst	triclinic	Triclinic	trigonal	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}c$	$C2/c$
a (Å)	10.869(5)	11.629(2)	24.386(3)	24.961(5)
b (Å)	14.314(2)	12.226(2)	24.386(3)	19.972(4)
c (Å)	14.428(2)	13.236(3)	24.386(3)	17.653(4)
α (deg)	118.440(10)	70.69(3)	44.76(2)	90
β (deg)	92.97(2)	67.27(3)	44.76(2)	129.55(3)
γ (deg)	93.93(2)	71.76(3)	44.76(2)	90
V (Å^3)	1960.0(10)	1600.5(5)	6541.0(4)	6785.7(25)
Z	2	1	4	4
ρ_{calcd} (g cm^{-3})	1.347	1.485	1.663	1.778
μ (mm^{-1})	0.623	0.754	1.086	1.239
temp (K)	293(2)	293(2)	293(2)	293(2)
R^a	0.0734	0.0772	0.0773	0.0684
$R_w{}^b$	0.1741	0.2338	0.2122	0.1860

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [(\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2)]^{1/2}$.

frame.[9] A self-consistent semiempirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using ABSCOR.[10]

All the structures were solved by direct methods using SHELXS-86[11] and refined by a full-matrix least-squares using SHELXL-93.[12] Most of the non-hydrogen atoms were subjected to anisotropic refinement except those discussed below. The hydrogen atoms were included in structure factor calculations using isotropic thermal parameters but not refined. The function minimized was $\sum w(F_o{}^2 - F_c{}^2)$, with $w = [\sigma^2(F_o{}^2) + aP^2 + bP]^{-1}$, where $P = [(F_o)^2 + 2F_c{}^2]/3$.

Some of the anions and solvent molecules were found to exhibit disorder. In complex **1**, the two uncoordinated oxygen atoms and the three fluorine atoms of the $CF_3SO_3{}^-$ anion exhibit disorder over two locations and were refined isotropically with half-site occupancy. The solvent water molecule exhibited an abnormally high thermal parameter and was isotropically refined with a fractional site occupancy factor of 0.25. The $CF_3SO_3{}^-$ anion in complex **2** showed a similar disordered pattern. Three fluorine atoms and one oxygen atom were disordered between two slightly different locations and were isotropically refined with partial occupancies. Two independent sites were modeled for the water molecule with total occupancies equal to unity. No hydrogen atoms were included. One perchlorate of complex **3** is located on a 2-fold axis and hence exhibits 2-fold orientational disorder with occupancy factors of 0.3 and 0.7. There is a highly disordered methanol solvate molecule in complex **3**; the oxygen atom occupies a site of symmetry 3 and the carbon atom exhibits disorder in opposite directions, thus showing axial disorder in six positions with total occupancy factors equal to 1. In complex **4**, the three fluorine atoms of the coordinated $CF_3CO_2{}^-$ anion were axially disordered about the C−C bond and were isotropically refined with half occupancy. The other uncoordinated one was disordered in such a way that the CF_3 group occupied two positions. Each was isotropically refined with the occupancy factors of every atom adding to 1. A summary of crystal data is given in Table 1. Selected bond distances and bond angles are listed in Table 2. Further details and Figures 5−11 are presented in the Supporting Information.

Results and Discussion

Synthesis and General Properties. Reactions of the appropriate acids with *o*-phenylenediamine have been proved to be a useful method to prepare substituted benzimidazole functional groups.[13] The ligand tris(2-benzimidazolylmethyl)-amine (ntb) has been synthesized long ago[7] using this method, and further reaction with alkyl iodide yields *N*-substituted derivatives,[8] which are unambiguously identified by H[1] NMR. A free ligand of this type possesses C_3 symmetry with three benzimidazole arms lying on the same side as show in Chart 1. Two conformations may predominate: the endo comformation

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds **1**−**4**[a]

Compound **1**			
Ag(1)−N(4)	2.359(2)	Ag(1)−N(6)	2.372(3)
Ag(1)−N(2)	2.372(3)	Ag(1)−O(11)	2.561(5)
N(4)−Ag(1)−N(2)	109.92(10)	N(4)−Ag(1)−O(11)	96.22(12)
N(4)−Ag(1)−N(6)	108.27(10)	N(2)−Ag(1)−O(11)	130.64(14)
N(2)−Ag(1)−N(6)	104.16(10)	N(6)−Ag(1)−O(11)	106.2(2)
Compound **2**			
Ag(1)−N(6)	2.231(3)	Ag(1)−N(2A)	2.253(3)
Ag(1)−N(4A)	2.252(3)	Ag(1)−Ag(1A)	2.8827(9)
N(6)−Ag(1)−N(4A)	122.21(10)	N(6)−Ag(1)−Ag(1A)	131.63(8)
N(6)−Ag(1)−N(2A)	109.22(11)	N(4A)−Ag(1)−Ag(1A)	79.87(9)
N(4A)−Ag(1)−N(2A)	117.90(10)	N(2A)−Ag(1)−Ag(1A)	91.30(9)
Compound **3**			
Ag(1)−N(2)	2.075(3)	Ag(1)−Ag(1A)	3.1065(14)
Ag(1)−N(6)	2.096(3)	Ag(1)−Ag(1B)	3.1065(14)
N(2)−Ag(1)−N(6)	158.99(8)	N(2)−Ag(1)−Ag(1B)	77.11(5)
N(2)−Ag(1)−Ag(1A)	121.00(7)	N(6)−Ag(1)−Ag(1B)	121.83(6)
N(6)−Ag(1)−Ag(1A)	79.08(5)	Ag(1A)−Ag(1)−Ag(1B)	60.0
Compound **4**			
Ag(1)−N(5)	2.128(3)	Ag(2)−N(3)	2.170(3)
Ag(1)−N(5A)	2.128(3)	Ag(3)−N(1)	2.217(3)
Ag(1)−Ag(3)	3.335(2)	Ag(3)−N(8)	2.303(4)
Ag(1)−Ag(3A)	3.335(2)	Ag(3)−O(21)	2.476(4)
Ag(2)−N(3A)	2.170(3)	Ag(3)−O(22)	2.546(3)
N(5)−Ag(1)−N(5A)	164.28(13)	N(1)−Ag(3)−N(8)	116.50(11)
N(5)−Ag(1)−Ag(3)	66.00(5)	N(1)−Ag(3)−O(21)	122.93(14)
N(5A)−Ag(1)−Ag(3)	116.45(5)	N(8)−Ag(3)−O(21)	116.67(15)
N(5)−Ag(1)−Ag(3A)	116.45(5)	N(1)−Ag(3)−O(22)	117.03(12)
N(5A)−Ag(1)−Ag(3A)	66.00(5)	N(8)−Ag(3)−O(22)	117.08(13)
Ag(3)−Ag(1)−Ag(3A)	163.71(2)	O(21)−Ag(3)−O(22)	49.45(10)
N(3A)−Ag(2)−N(3)	152.58(14)	N(1)−Ag(3)−Ag(1)	70.57(5)
N(8)−Ag(3)−Ag(1)	117.18(7)	O(22)−Ag(3)−Ag(1)	57.07(7)
O(21)−Ag(3)−Ag(1)	101.69(9)		

[a] Symmetry transformation used to generate equivalent atoms. For **2**, (A) $-x, -y, -z$. For **3**, (A) $z - 1, x, y + 1$; (B) $y, z - 1, x + 1$. For **4**, (A) $-x, y, -z - 0.5$.

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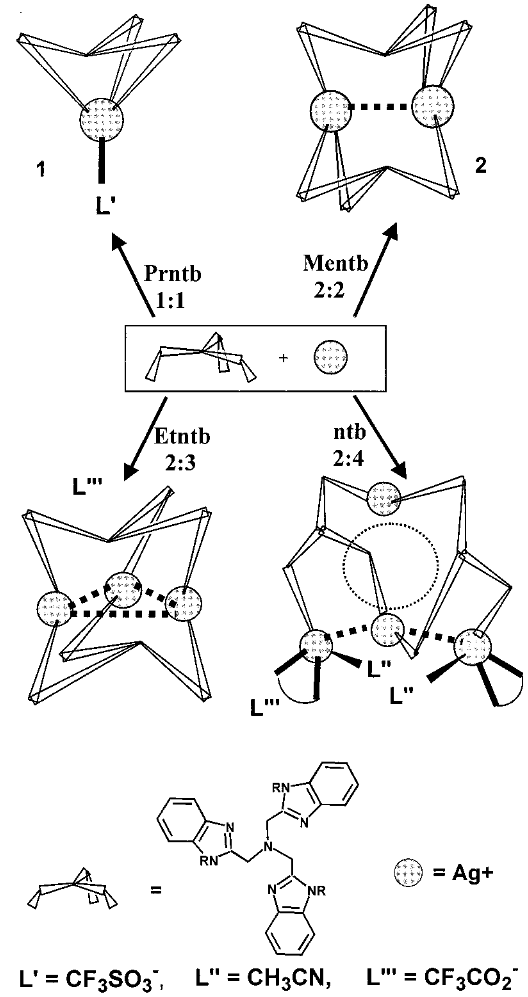
Chart 2



with three imine N atoms pointing inward at the lone electron pair of the apical tertiary nitrogen atom and, otherwise, the exo conformation. Interconversion of these two conformations can be easily achieved through rotation of three benzimidazole arms about the respective $N_{apical}-C$ bonds and/or the well-known inversion of the tetrahedral tertiary amine (three bonds and one lone pair). Since the $N_{apical}-C$ bond is of entirely single bond character, the rotation of the three arms should be virtually free. When an approximate 5 kcal mol^{-1} activation energy is allowed for the inversion of a tertiary amine, the interconversion energy barrier for the two conformations should not exceed 10 kcal mol^{-1}. This means that the free ligand may take an arbitrary conformation and that interconversion is facile in solution. That the NMR spectra of all four ligands display only a single set of proton signals at room temperature evidently supports this estimation. On crystallization, the adopted conformation may be difficult to predicate but is surely related to the crystal packing mode or interactions between imine N atoms and solvent molecules. X-ray analysis has shown that Prntb takes the exo conformation[4b] while ntb takes the endo conformation because of inclusion of a water molecule.[14] Such findings suggest that C_3-symmetric tripodal ligands of this type may interact with metal ions in diversified forms, inspiring us to investigate their coordination behavior with silver(I) and the effect of the counteranions and *N*-substituted alkyl groups on the coordination geometry and crystal packing. Four complexes were readily obtained from one-pot reactions of the tripodal ligands with different silver(I) salts (Chart 2). Elemental analyses led to stoichiometric formulas of the four complexes: $Ag(CF_3SO_3)(Prntb)(0.25H_2O)$, **1**, $Ag(CF_3SO_3)(Mentb)(0.5H_2O)$, **2**, $[Ag(ClO_4)]_3(Etntb)_2(CH_3OH)$, **3**, and $[Ag(CF_3CO_2)]_2(ntb)(CH_3CN)(H_2O)$, **4**. Single-crystal X-ray analyses showed that **1** is monomeric $[Ag(Prntb)(CF_3SO_3)]\cdot 0.25H_2O$, **2** is dimeric $[Ag_2(Mentb)_2](CF_3SO_3)_2\cdot H_2O$, **3** is trinuclear $[Ag_3(Etntb)_2](ClO_4)_3\cdot CH_3OH$, and **4** is tetranuclear $[Ag_4(ntb)_2(CF_3CO_2)_2(CH_3CN)_2](CF_3CO_2)_2\cdot 2H_2O$. The formation of mono- to tetranuclear complexes is profoundly influenced by various factors such as the metal-to-ligand ratio, the coordinating nature of the anions, the substituent R, and the conformation of the ligand. For a tripodal ligand with three potential nitrogen donors on its arms, the generation of a mononuclear complex can be rationalized when the metal-to-ligand ratio is no more than 1:1. However, the formation of polynuclear structures is more complicated and may be governed by the coordinating nature of the anions. The $CF_3CO_2^-$ anion exhibits strong coordination ability toward Ag(I), while the ClO_4^- anion tends to be nonligating. The $CF_3SO_3^-$ anion shows somewhat weaker binding ability, often acting as an auxiliary ligand to fulfill the remaining coordination site (for example, as in **1**). Thus, the reaction using silver(I) perchlorate or triflate[4d] in 2:3 ratio affords trinuclear complexes with the counteranions free from coordination, but when the $CF_3CO_2^-$ salt is used in more than 2:3 molar ratio, a tetranuclear complex or coordination polymer[14] is formed in which the anion functions as either a chelating ligand or a bridging auxiliary ligand. The substituent group R also plays an important role in the formation of polynuclear structures; as in the case of the Mentb ligand, the formation of a dinuclear complex is preferred over other combinations using either $CF_3SO_3^-$ or ClO_4^-. Overall, the outcome of the reaction is often influenced by more than one factor, but in principle, one tripod ligand can hold one Ag(I) ion and two ligands in endo conformation can encapsulate up to three Ag(I) ions. Generating structures of higher nuclearity has to take advantage of the exo conformation and will be discussed in the structural section below. All of the complexes showed no photosensitivity when stored in air for a long time, of which **1**−**3** are air-stable and **4** effloresces slowly on exposure to air. The existence of the water (or methanol in **3**) solvate molecules may also be confirmed by the appearance of a broad band around 3400 cm^{-1} in their IR spectra. The absorption at 2334 cm^{-1} is assigned to the stretching vibration of $C\equiv N$, which indicates that there are CH_3CN molecules in complex **4**. Information regarding the possible bonding modes of the anions may also be obtained from the IR spectra. Two single bands observed at about 1261 and 1028 cm^{-1} in complex **2** are tentatively assigned to asymmetric and symmetric SO_3 stretching modes, respectively, which are closely similar to those found for the free $CF_3SO_3^-$ ion.[15] In complex **1**, the $\nu_{as}(SO_3)$ band splits into two bands at 1281 and 1253 cm^{-1}, indicating that the $CF_3SO_3^-$ ion is involved in coordination, although we could not distinguish whether it is monodentate or bidentate because the highest symmetry for both is C_s.[15] The absorption bands appearing at 1091 (ν_3) and 622 cm^{-1} (ν_4) in complex **3** are characteristic of an uncoordinated perchlorate ion.[16] In the IR spectrum of **4**, the strong broad band at 1668 cm^{-1} is assigned to the ν_{as} vibration and the somewhat weak band at 1450 cm^{-1} to the ν_s vibration of the $CF_3CO_2^-$ anion. The separation ($\Delta =$

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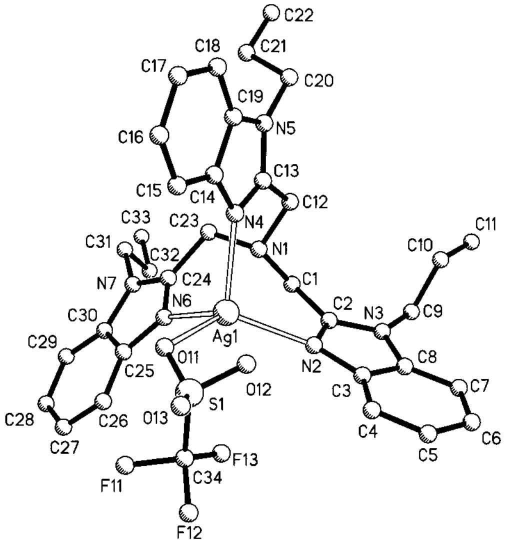

Figure 1. Perspective view and atom labeling of the [Ag(Prntb)(CF_3SO_3)] molecule in complex **1**.

219 cm^{-1}) and energy level observed suggest the chelating mode for the $CF_3CO_2^-$ anion.[17] However, the single-crystal analysis showed that both chelating and uncoordinated $CF_3CO_2^-$ anions coexist in the complex. Since two oxygen atoms of the uncoordinated $CF_3CO_2^-$ form hydrogen bonds in the crystal lattice, which would be expected to reduce the separation between ν_{as} and ν_s vibrational bands,[17b] the absence of bands due to the uncoordinated $CF_3CO_2^-$ group can be rationalized.

Descriptions of Crystal Structures. The crystal structure of complex **1** shows a discrete neutral [Ag(Prntb)(CF_3SO_3)] molecule in which Prntb adopts an endo conformation with its apical nitrogen atom pointing inward, thus acting as a tridentate ligand with its three imidazole nitrogen atoms coordinated to the silver(I) ion. From Figure 1 it may be seen that the three benzimidazole arms wrap around a cavity with the silver(I) ion located in the center and that the fourth coordination site is filled by one oxygen atom of the $CF_3SO_3^-$ anion. A similar distorted tetrahedral coordination environment was also found in silver(I) complexes containing pyrazolylborate tripodal ligands.[18] The largest deviation from the normal tetrahedral coordination at Ag(1) arises from the angles of N(4)−Ag(1)−O(11) (96.2 (1)°) and N(2)−Ag(1)−O(11) (130.6 (1)°). This may be caused by the weak interaction of the oxygen atom O(12) that dangles above N(2) and N(4) at a distance of 2.725 Å from Ag(1). The Ag−N bond distances (Ag(1)−N(2), 2.372(3) Å; Ag(1)−N(4), 2.359(2) Å; Ag(1)−N(6), 2.372(3) Å) are similar to those of Ag−N(pyrazole) bonds (ranging from 2.353 to 2.408 Å)[18] but longer than those of Ag−N(pyrimidine) bonds (2.271 Å).[19] The Ag−O bond distance is 2.561(5) Å, and similar (2.536 Å)[20] or shorter (2.264 Å)[18a] Ag−O bond distances of the triflate anion were observed in other complexes.

Complex **2** consists of a binuclear [$Ag_2(Mentb)_2$]$^{2+}$ cation, two free $CF_3SO_3^-$ anions, and a lattice water molecule. The molecular structure of the centrosymmetric binuclear cation is shown in Figure 2. The Mentb ligand adopts an endo conformation and also behaves as a tridentate ligand in the bridging mode. Thus, each Ag(I) ion is bonded by two benzimidazole arms of one Mentb and one benzimidazole arm of the other, resulting in an encapsulated, trigonally coordinated environment. However, the Ag(I) ions are each displaced by 0.427 Å from the plane defined by the three nitrogen donors toward the other, leading to a short Ag···Ag distance of 2.8817(9) Å, which is nearly equal to that in metallic silver (2.89 Å). This type of Ag···Ag interaction[2h,21] may be responsible for the aggregation of the two Mentb ligands to generate the binuclear complex. Among other reported trigonally coordinated binuclear silver(I) complexes[22] with nitrogen donors, all have much longer Ag···Ag distances except one with a shorter Ag···Ag distance of 2.762 Å.[22e] The Ag−N bond distances are unremarkable at 2.231(3) and 2.253(3) Å, being slightly shorter than those of four-coordinate Ag(I) in **1.**

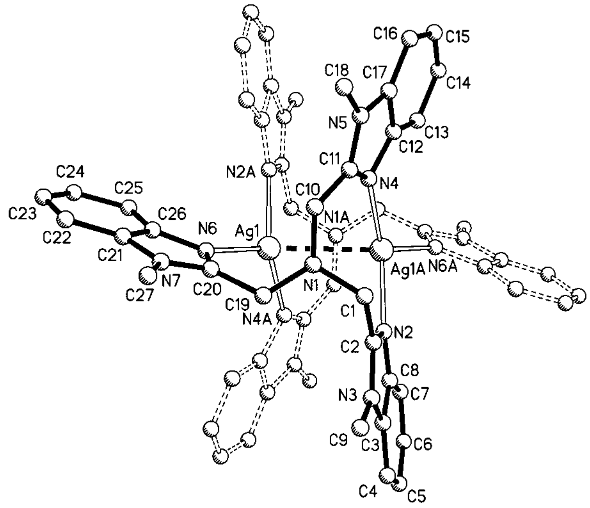

Figure 2. Perspective view and atom labeling of the [$Ag_2(Mentb)_2$]$^{2+}$ cation in complex **2.** The C_2 molecular axis runs vertically and passes through the midpoint of the dotted line between Ag(1) and Ag(1a).

X-ray analysis of **3** showed that the complex consists of a trinuclear cation [$Ag_3(Etntb)_2$]$^{3+}$, three perchlorates, and one methanol solvate molecule. The molecular structure of the [$Ag_3(Etntb)_2$]$^{3+}$ cation depicted in Figure 3 exhibits some similarity to that in complex **2**. Two endo Etntb tripodal ligands are aggregated by the coordination of their imidazole nitrogen atoms to silver(I) ions to form a sandwiched structure. But in this case, each ligand attaches one arm to a corner of a regular triangular array of Ag(I) ions. The 3-fold symmetry axis passes through the center of the Ag_3 triangle and the apical nitrogen atoms of the two Etntb ligands lying above or below the Ag_3 plane. Each Ag(I) ion has an identical bent[6] coordination geometry with an N−Ag−N angle of 158.99(8)°. This bent coordination geometry sometimes has been considered to be the consequence of weak coordination to neighboring ligands,[6] but in the present case there is only the possibility of weak Ag···Ag interaction at

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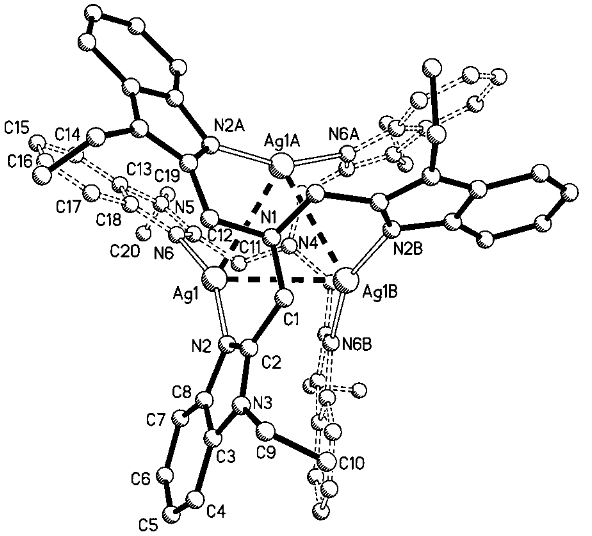

Figure 3. Perspective view and atom labeling of the $[Ag_3(Etntb)_2]^{3+}$ cation in complex **3.** The C_3 molecular axis passes through atoms N(1) and N(4) and the center of the Ag_3 triangle.

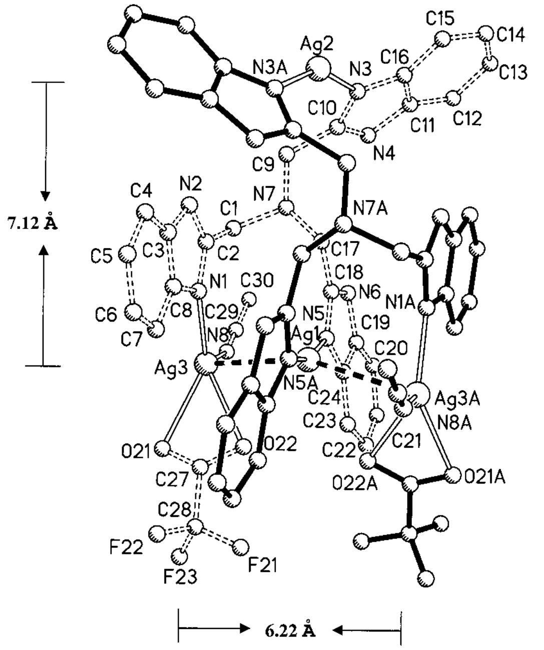

Figure 4. Perspective view and atom labeling of the $[Ag_4(ntb)_2(CF_3CO_2)_2(CH_3CN)_2]^{2+}$ cation in complex **4.** The C_2 molecular axis runs vertically and passes through atoms Ag(1) and Ag(2).

3.1065(14) Å. Although the nature of the Ag···Ag interaction is not clearly understood, Ag(I) clusters are often formed even if the Ag···Ag separation may exceed the interatomic distance in metallic silver (2.89 Å).[2a,21] One known example is the $(Ag^+)_6$ cluster formed in the complex $[Ag(imidazole)_2](ClO_4)$[23] in which there is also a Ag_3 cluster with an Ag···Ag separation of 3.493(1) Å with no other bridge. Therefore, the present complex may be regarded as a trinuclear Ag(I) cluster sandwiched or encapsulated by two tripodal ligands. The Ag−N bond distances (2.075(3)−2.096(3) Å) show unremarkable features and closely resemble those in linearly coordinated Ag(I) imidazole complexes[23] but are obviously shorter than those in **1** and **2**.

Figure 4 shows the molecular structure of the $[Ag_4(ntb)_2(CF_3CO_2)(CH_3CN)_2]^{2+}$ cation in complex **4**. The construction of the tetranuclear cation, which lies on a 2-fold axis, involves two ntb ligands, two auxiliary $CF_3CO_2^-$ anions, and an acetonitrile ligand. Contrary to the endo conformation in **1**−**3**, the tripodal ligand ntb in **4** adopts the exo conformation such that its three benzimidazole arms are fully extended to coordinate to three different kinds of silver(I) ions: Ag(1) and Ag(2) both lying on the molecular symmetry axis, and Ag(3) which is further coordinated by an acetonitrile molecule and two chelate oxygen atoms of a trifluoroacetate anion. Thus, in the resulting tetranuclear cation, the silver(I) ions have two kinds of coordination geometry, namely, linear for Ag(1) and Ag(2) and tetrahedral for Ag(3) and Ag(3a). The tetrahedral geometry of Ag(3) exhibits severe distortion mainly because of the small bite angle of the bidentate CO_2^- group, and the Ag(1)···Ag(3) separation is 3.335(2) Å. The Ag−N bond distances (Ag(1)−N(5), 2.128(3) Å; Ag(2)−N(3), 2.170(3) Å) of the two linearly coordinated Ag(I) ions are slightly longer than that in **3** with a similar coordination mode but are obviously shorter than those with trigonal or tetrahedral coordination geometry in **1** and **2**. However, the tetrahedrally coordinated Ag(3) gives a somewhat shorter Ag(3)−N(1)(benzimidazole) bond distance of 2.217(3) Å perhaps because of the less rigid steric environment. The Ag(3)−N(8)(acetonitrile) bond distance of 3.303(4) Å lies well within the reported range of bond distances.[24] The Ag−O bond distances (2.476(4) and 2.546(3) Å) are also normal for bidentate trifluoroacetatesilver(I) complexes.[25]

The above discussion shows the versatility of the present C_3-symmetric tripodal ligands for the aggregation of silver(I) complexes. With reference to the scheme shown in Chart 2, four complexes from mononuclear to tetranuclear have been synthesized in which diverse coordination modes and coordination geometries have been found. In the endo conformation, a tripodal ligand can use its three benzimidazole arms to embrace a silver(I) ion to produce a monomeric complex (**1**). The arms can also splay out slightly to encapsulate a di- or trinuclear silver(I) system (**2**, **3**). Most importantly, they can even rotate freely around the N_{apical}−C bonds to adopt an exo conformation, thus facilitating the generation of a cagelike complex (**4**) or a coordination polymer.[14] Since one of our primary objectives is to construct multicomponent structures with possibly an internal cavity, we are particularly interested in the metal-directed aggregation of the ligands. If the ligands adopt the endo conformation, they seem to prefer to accommodate metal ions in their own cavity. So complexes **2** and **3** may be seen as a silver(I) dimer and trimer, respectively, coupled by two tripodal ligands. The weak Ag···Ag interactions may also contribute to the stability of such sandwiched structures. In this sense, a cagelike structure could only be constructed by a larger "splaying out" of the three arms, and metal ions with insignificant metal−metal interaction should be used. However, this is not the case if the exo conformation is adopted. If the auxiliary ligands are neglected, **4** may be considered as a six-component cage comprised of two tripodal ligands bridged by four Ag(I) ions (Figure 4). The four silver(I) atoms are arranged in a T-shape array, and two benzimidazole moieties approach from opposite sides to close the cavity. The size of the internal core may be estimated by the separation of 7.12 Å between Ag(1) and Ag(2) and the centroid−centroid distances of 6.22 Å between two nearly parallel benzimidazole rings, which com-

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pares well with other reported multicomponent three-dimensional cages.[2]

Crystal Packing. Weak supramolecular $\pi\cdots\pi$ and CH$\cdots\pi$ interactions play important roles in the crystal packing modes in **1**−**3**, while in **4** the somewhat strong NH$\cdots$O and OH$\cdots$O hydrogen bonds are dominant. Figures 5−11, which illustrate the packing modes, are given as Supporting Information.

In the mononuclear complex **1**, the tripodal Prntb ligand wraps around the Ag(I) ion in such a way that on viewing down from the apical nitrogen atom to the Ag(I) ion, the Prntb ligand shows either a right- or left-handed propeller appearance. This type of arrangement in the helical sense is intrinsically chiral[5b] and will result in a pair of enantiomers. With all three *N*-propyl groups pointing in the same direction, embracing the $CF_3SO_3^-$ group of an adjacent molecule, the head-to-tail arrangement of molecules of the same handedness in **1** results in a chiral column as shown in Figure 5. Each column is surrounded by three other columns of opposite chirality in an antiparallel manner, generating a hexagonal channel running parallel to the *a* axis (inner linear dimension of ca. 8.32 Å between the nearest atoms) in which the highly disordered solvent water molecules are lodged (Figure 6). Such an array of columns may be stabilized by aryl−aryl interactions between benzimidazole rings. As shown by a projection on the *bc* plane in Figure 7, each tripodal arm of an individual molecule is involved in three aryl−aryl interactions with three adjacent benzimidazole rings from neighboring columns; one is an offset $\pi\cdots\pi$ stacking at distances in the range 3.668−3.813 Å, and the other two are edge-to-face interactions with centroid−centroid distances ranging from 5.042 to 5.071 Å.[3,26] Thus, each molecule within a column is locked by three molecules from adjacent columns with a total of nine aryl−aryl interactions.

Complex **3** exhibits a crystal packing somewhat similar to that of **2**. Instead of offset and edge-to-face $\pi\cdots\pi$ stacking interactions in **2**, the crystal packing of **3** is controlled by methyl-to-aryl (CH$\cdots\pi$)[3,26,27] and edge-to-face interactions, as shown in Figure 8. Two independent Etntb ligands above and below the triangular Ag_3 plane show both kinds of interactions but in different ways. For one ligand, the ethyl group of a tripodal arm forms a CH$\cdots\pi$ interaction of 3.568 Å with an adjacent molecule, while the benzimidazole ring forms an edge-to-face interaction at 5.188 Å with another adjacent molecule. For the other ligand, only the benzimidazole rings are involved in methyl-to-aryl and aryl-to-aryl interactions at the same distances. Therefore, every molecule is surrounded by six CH$\cdots\pi$ and six $\pi\cdots\pi$ interactions to generate a honeycomb layer in the (111) plane as shown in Figure 9, and the sandwich arrangement of such layers in the crystal lattice leaves large voids to be occupied by the perchlorate anions and methanol solvate molecules.

Figure 2 shows that in complex **2** the two Mentb ligands have two pairs of closely adjacent benzimidazole rings, which exhibit weak intramolecular $\pi\cdots\pi$ stacking interactions at a distance of 3.956 Å. The remaining two benzimidazole rings belonging to different ligands point in opposite directions and are nearly perpendicular to the other two pairs. This spatial arrangement of the two ligands accounts for the fact that the methyl group exerts a great influence on the crystal packing of **2**. The methyl-to-aryl interactions appear in pairs between every two neighboring molecules, and each molecule is involved in four pairs of such CH$\cdots\pi$ interactions in four directions (Figure 10). A squarelike two-dimensional network is thus observed in the *ab* plane with the square cavity filled by uncoordinated anions and water molecules.

In complex **4** the unsubstituted NH group is a potential hydrogen bond donor, which together with the water molecule generates N$\cdots$O and O$\cdots$O hydrogen bonds as the dominant packing forces. Figure 11 shows the hydrogen-bonding pattern in the crystal lattice. Although all six NH groups and two oxygen atoms from two coordinated $CF_3CO_2^-$ anions participate in the formation of hydrogen bonds, there is essentially only one hydrogen bonding bridge consisting of one water molecule and one uncoordinated $CF_3CO_2^-$ anion. Every bridge of this type connects three different molecules through five hydrogen bonds; the water molecule forms three hydrogen bonds with one oxygen atom of the bidentate $CF_3CO_2^-$ anion (O$\cdots$O, 2.776 Å), with a NH group (O$\cdots$N, 2.696 Å) from a different molecule, and with one oxygen atom of the uncoordinated $CF_3CO_2^-$ anion (O$\cdots$O, 2.723 Å). The other oxygen atom of the uncoordinated $CF_3CO_2^-$ anion further forms two hydrogen bonds with two NH groups of the third molecule (O$\cdots$N, 2.822 and 2.828 Å). The whole crystal structure may be regarded as a three-dimensional hydrogen-bonded network joined by this hydrogen-bonding bridge.

Conclusion

The present work demonstrates that the C_3-symmetric tripodal ligand tris(2-benzimidazolylmethyl)amine and its *N*-substituted derivatives constitute a class of versatile ligands for the construction of various silver(I) aggregates. Four complexes from mononuclear to tetranuclear have been synthesized in which the ligands all behave as tridentate ligands with imidazole nitrogen atom donors, and the silver(I) atoms show various coordination modes of linear (or bent), trigonal, and tetrahedral geometries. The ability of the three benzimidazole arms to freely rotate about the N_{apical}−C bonds permits the ligand to adopt either the endo or the exo conformation. In the endo case the tripod ligand may use its pendant arms to embrace a single silver(I) atom or may act in pairs to form sandwiched bi- or trinuclear silver(I) clusters with weak Ag$\cdots$Ag interactions. However, the exo case facilitates the construction of large multicomponent structures that may possess an internal cavity. By a judicious choice of auxiliary ligands and/or counterions, the generation of nanoscale molecular aggregates may be explored. The mode of crystal packing is obviously influenced by diverse intermolecular interactions. With N-substituted ligands, $\pi\cdots\pi$ and CH$\cdots\pi$ interactions are the main packing forces and a honeycomb layer, a square channel, or a hexagonal channel is formed to accommodate the solvate molecules and counterions. In the presence of the hydrogen donor group NH, somewhat stronger NH$\cdots$O and OH$\cdots$O hydrogen bonds play dominant roles in the crystal packing.

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Supporting Information Available: Figures 5−11 and X-ray crystallographic files, in CIF format, for the structure determinations of complexes **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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