

4,4'-BIPYRIDINE-2,2',6,6'-TETRACARBOXAMIDE. SYNTHESIS AND SELF-ASSEMBLING PROPERTIES OF THE FREE BASE AND THE 1 : 1 SILVER(I) TRIFLATE COMPLEX

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Received June 7, 2002
Accepted June 28, 2002

Self-assembly of 4,4'-bipyridine-2,2',6,6'-tetracarboxamide and its 1 : 1 silver(I) triflate complex was investigated by single crystal X-ray diffraction analysis. It was found that intermolecular amide–amide hydrogen bonds control the crystal packing of the free base giving rise to infinite zig-zag tapes, whereas an octahedral coordination of the Ag(I) ion with the ligand dominates in the packing of the corresponding complex.

Keywords: X-Ray diffraction; Hydrogen bonds; Transition metals; Supramolecular chemistry; Amides; Biaryls; Bipyridines; Crystal engineering; Self-assembly.

Design of microporous solids *via* supramolecular self-assembly of complementary subunits (tectons) is a subject of growing interest^{1–5}. Our recent discovery^{6–8} that biphenyl-2,2',6,6'-tetracarboxylic acid **1** as well as the corresponding tetraamide **2** self-assemble under formation of 2D layers set up from cyclotetrameric hydrogen-bonded open-square compartments (Fig. 1) may be pertinent to this challenging problem. As we already pointed out elsewhere^{6,9}, eclipsed stacking of the self-assembled 2D biaryl layers (Fig. 2a) could provide access to a variety of achiral as well as chiral microporous solids.

X-Ray structure analysis of both the parent biaryl tectons **1** and **2**, however, shows^{6–8} that the resulting 2D layers are preferentially stacked in a staggered manner in the crystal lattice (Fig. 2b). In this arrangement, cavities inside the individual square compartments are filled with the aryls protruding from the neighboring layers, which obstructs formation of the micropores.

In order to promote the eclipsed stacking of the 2D layers, additional “sticking” substituents have been introduced into the 4,4'-positions of the parent biaryl tecton **1**, so far without the expected effect⁷. In the present paper, we have combined the concept of “sticking” substituents with the coordinating potential of transition metal ions. Monovalent silver(I) ions

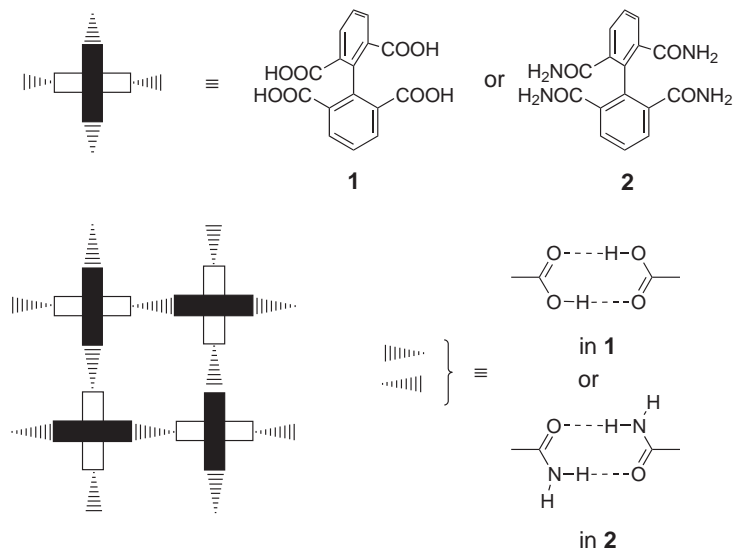


FIG. 1
Cyclotetrameric hydrogen-bonded square compartments in the crystal structure of tetraacid **1** and tetraamide **2**

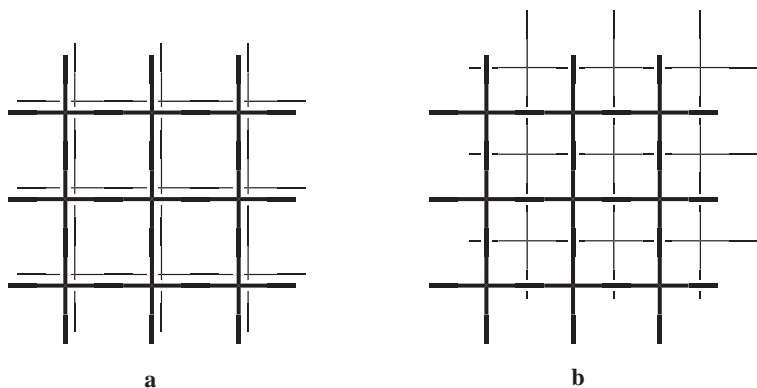


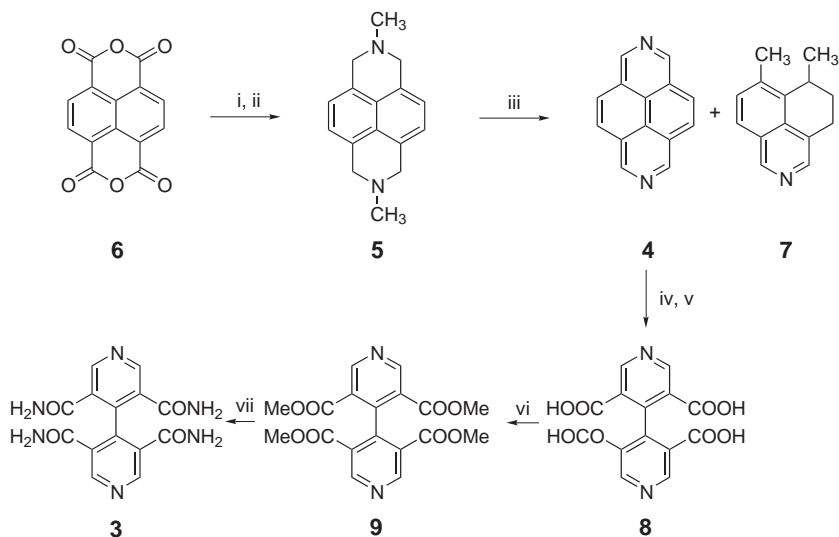
FIG. 2
The eclipsed (a) and staggered (b) stacking of 2D layers set up from square compartments

rank among the few metal ions securing a linear bidentate coordination. The ability of the linear pyridine...Ag(I)...pyridine coordination to operate in the presence of hydrogen-bonded CO-NH₂ grouping has been recently demonstrated¹⁰ in the silver complex of nicotinamide. In the complex, the silver(I) ion coordinates with the ligand molecules solely through the pyridine nitrogen atoms, whereas the carboxamide groupings are engaged in the formation of intermolecular amide-amide double hydrogen bonds. On such grounds, we have chosen 4,4'-bipyridine-2,2',6,6'-tetracarboxamide **3** and its 1 : 1 complex with silver(I) triflate as the subject of the present study.

RESULTS AND DISCUSSION

Synthesis

Retrosynthetic analysis of the novel bipyridine tetraamide **3** points to 2,7-diazapyrene **4** as the most convenient synthon (Scheme 1) which is



- i : aq. CH₃NH₂, 100 °C, 3 h
 ii : AlCl₃/LiAlH₄, THF, reflux, 4 h
 iii : 10% Pd/C, 320 °C, 1 h
 iv : KMnO₄, NaOH, H₂O, 80 °C, 1 h
 v : aq. HCl
 vi : CH₂N₂/ether/DMF, r.t., 2 h
 vii: NH₂/CH₃OH, r.t., 5 days

SCHEME 1

available from the commercial dianhydride **6** by a two-step literature procedure¹¹. Hitherto unknown 6,7-dimethyl-5,6-dihydro-4*H*-benzo[*de*]isoquinoline **7** was isolated as the major side product in the preparation of **4**, arising presumably by hydrogenolysis of one of the heterocyclic rings of the intermediate diamine **5**. As expected, oxidative cleavage of **4** with potassium permanganate gave 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid **8** which could be smoothly converted, *via* the tetraester **9**, into the target tetraamide **3** and its silver(I) triflate complex.

Crystal Structure of the Free Bipyridine Tetraamide **3**

The molecular structure of the tetraamide **3** was determined by X-ray crystallographic analysis of the corresponding trihydrate (Fig. 3a). The established bond angles and distances are unexceptional. Each of pyridine rings is essentially planar, the deviation from planarity being less than 0.023 Å. The bipyridine axis, however, is bent at the central C₁-C_{1'} junction, the dec-

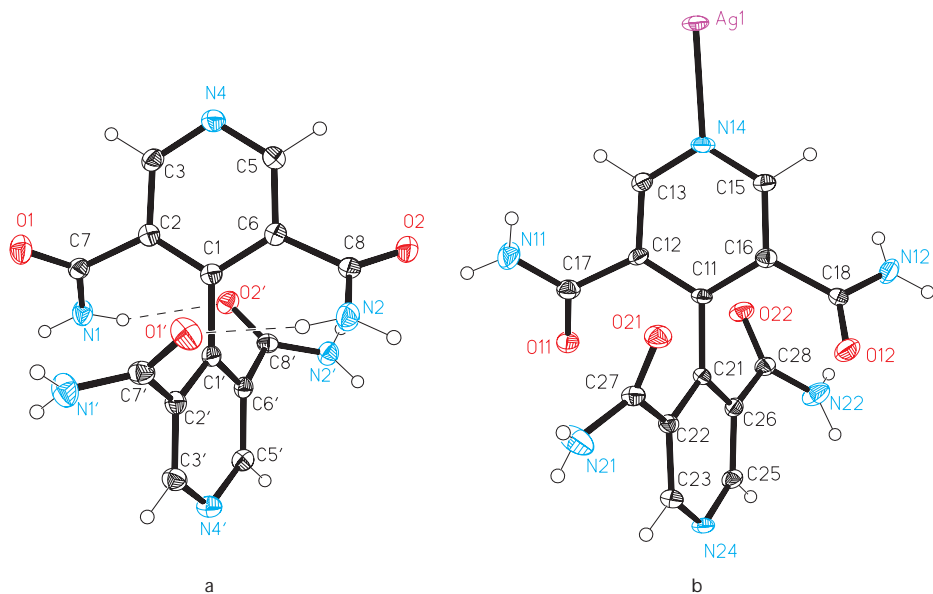


FIG. 3

Perspective views of the molecule of tetraamide **3** in the crystal of the free base (a) and in the crystal of its silver(I) triflate complex (b). Thermal ellipsoids are at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines

lination amounting to 0.135 Å at the central carbon atoms and 0.448 Å at the peripheral nitrogens. The dihedral angle between the coupled pyridine rings is 72.5°, resembling closely the value found⁸ for the biphenyl tetraamide analogue **2** (74.6 or 74.9°). The dihedral angles between the plane of the carboxamide grouping and the adjoined pyridine ring range between 49.8 and 57.8°, approaching the values 46.1–56.7° found for the biphenyl analogue **2**. Intramolecular hydrogen bonds pairwise connect the N–H and C=O portions of two carboxamide groupings placed at the opposite aryls in both the tetraamides **2** and **3**, which explains well similarity of their conformations.

In contrast, crystal packing of the two isosteric tetraamides **2** and **3** is entirely different. In the crystal of the biphenyl tetraamide **2**, double amide–amide hydrogen bonds organize formation of 2D layers set up from cyclotetrameric open squares⁸ (Fig. 1) whereas single amide–amide hydrogen bonds dominate in the packing of the bipyridine analogue **3** giving rise to infinite zig-zag tapes (Fig. 4). Each molecule participates in six such hydrogen bonds which, in triplets, provide supramolecular connection with the neighbors in the tape. Water molecules (inserted between amide groups or between pyridine nitrogens) connect the neighboring tapes under formation of the 3D hydrogen-bonded network (Fig. 5).

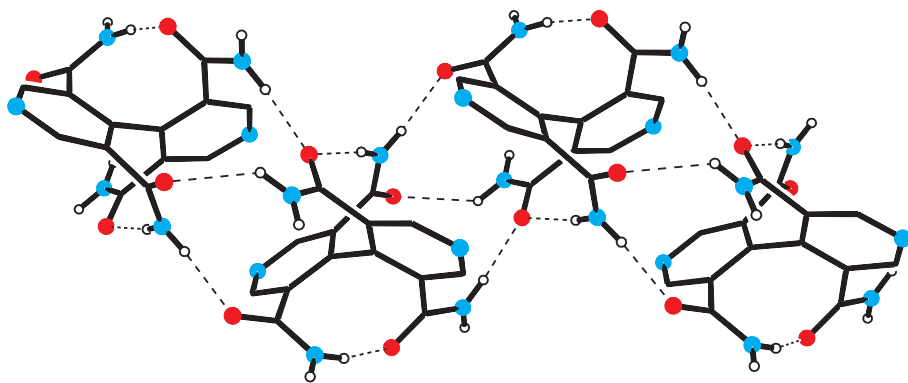


FIG. 4

Zig-zag tapes of molecules of the tetraamide **3** formed by single amide–amide hydrogen bonds (dashed lines). Oxygen and nitrogen atoms are drawn in red and blue, respectively, carbon atoms and C–H hydrogens are not depicted

Crystal Structure of the Ag(I) Complex

The bipyridine tetraamide **3** on treatment with silver(I) triflate affords the 1 : 1 complex which crystallizes from water in the form of trihydrate. From the crystallographic analysis it follows that the complexation does not much affect molecular structure of the bipyridine ligand **3** (Fig. 3b), diminishing somewhat the dihedral angle between the two pyridine rings (67.9°) as well as the dihedral angle between the plane of the amide grouping and the adjoining pyridine ring ($29.41\text{--}48.22^\circ$). Major changes concern mutual orientation of the individual amide groupings, which in the free ligand **3** is controlled by the requirements of hydrogen bonding whereas in the complexed ligand by coordination with the silver(I) ion.

Accommodation of the ligand molecules to the coordination sphere of Ag(I) ion is the key factor in the crystal packing of the investigated complex. In accord with expectation, pyridine-N...Ag(I)...N-pyridine interaction organizes the bipyridine molecules **3** into infinite linear chains (coordination bond lengths 2.237 and 2.240 Å, bond angle 173.8°). However, in contrast to the reported 2 : 1 nicotinamide–silver(I) triflate complex¹⁰, carbonyl donors in the tetraamide ligand **3** coordinate also with the silver(I) ion (coordination bond lengths Ag(I)...O 2.557, 2.675, 2.784 and 2.787 Å) giving rise to a quasi-octahedral coordination. In this way, the individual linear

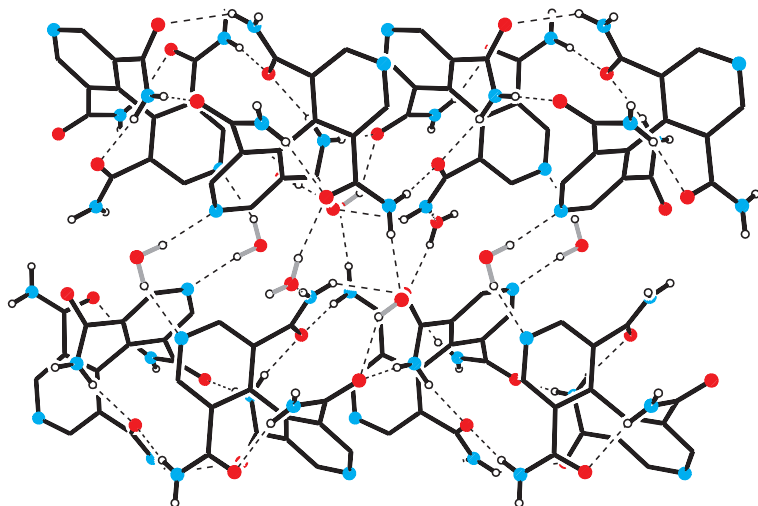


FIG. 5

Zig-zag tapes of molecules of tetraamide **3** interconnected by hydrogen bonds *via* water molecules (drawn with gray O–H bonds)

bipyridine chains are linked under formation of 2D planar layers (Fig. 6). Formation of intermolecular amide-amide hydrogen bonds (occurring in the nicotinamide complex¹⁰) is thus prohibited. The N-H groupings are turned out of the plane and link, *via* water molecule or triflate-ion-mediated hydrogen bonds, the neighboring 2D layers. No direct contacts occur between the Ag(I) and triflate ions.

In this way, self-assembly of 3D porous structure from biaryl tectons continues to be a challenge for further studies. Several alternative designs exploiting hydrogen bonds as well as transition metal ions are currently under study in our laboratory.

EXPERIMENTAL

Synthesis

Melting points were determined on a Kofler block and are uncorrected. ¹H NMR spectra were measured on a Varian Unity 200 spectrometer at 200 MHz, ¹³C NMR spectra on a Varian Unity 500 instrument at 125.7 MHz. Chemical shifts are given in ppm (δ -scale),

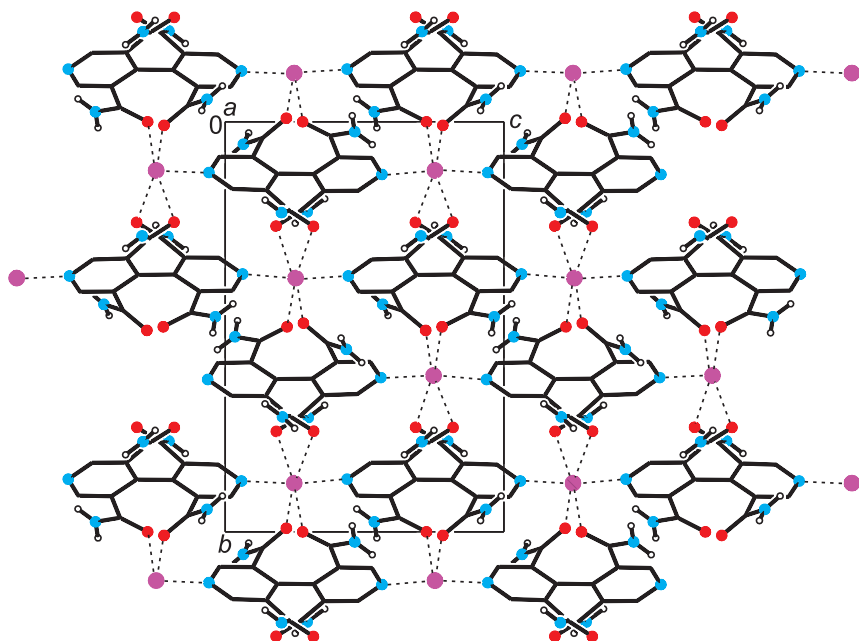


FIG. 6

Part of 2D layers in the crystal of $3\text{-CF}_3\text{SO}_3\text{Ag}$ formed by the coordination of the tetraamide molecules **3** to the Ag(I) ions (violet circles)

coupling constants (J) in Hz. Mass spectra were taken on a ZAB-EQ (VG Analytical) spectrometer in the EI (70 eV) or FAB mode (Xe, 8 kV, matrix: thioglycerol-glycerol (3 : 1) or bis(2-hydroxyethyl) sulfide).

6,7-Dimethyl-5,6-dihydro-4*H*-benzo[*de*]isoquinoline (7)

The title compound was isolated in 10% yield from first fractions in chromatography, following the aromatization¹¹ of 2,7-dimethyl-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline (5) to 2,7-diazapyrene (4); m.p. 93.5–95 °C (light petroleum). For C₁₄H₁₅N (199.3) calculated: 85.24% C, 7.66% H, 7.10% N; found: 84.63% C, 7.76% H, 6.91% N. ¹H NMR (200 MHz; CDCl₃): 1.24 d, $J = 7.1$ (14-H); 2.01 ddt, $J = 13.8, 13.0, 4.5, 4.5$ (12-H); 2.08 ddt, $J = 13.0, 5.2, 2.5, 2.5$ (12-H); 2.53 s (15-H); 2.95 dddd, $J = 16.5, 4.6, 2.5, 0.1$ (13-H); 3.19 dddd, $J = 16.5, 13.8, 5.1, 1.6, 1.6$ (13-H); 3.47 ddq, $J = 7.1, 7.1, 7.1, 4.5, 2.5$ (11-H); 7.38 d, $J = 8.3$ (8-H); 7.71 d, $J = 8.3$ (7-H); 8.29 dd, $J = 1.7, 0.6$ (6-H); 9.00 d, $J = 1.2$ (2-H). ¹³C NMR (125 MHz; CDCl₃): 18.99 q (14-C); 18.99 q (15-C); 21.78 t (13-C); 28.52 t (12-C); 29.55 d (11-C); 124.93 d (7-C); 127.14 s (5-C); 128.18 s (3-C); 130.35 d (8-C); 131.93 s (9-C); 135.55 s (4-C); 136.96 s (10-C); 140.92 d (6-C); 150.22 d (2-C). FAB MS, m/z : 198 [M + H]⁺.

4,4'-Bipyridine-3,3',5,5'-tetracarboxylic Acid (8)

Potassium permanganate (2.5 g, 15.8 mmol) was added portionwise to a suspension of 2,7-diazapyrene (4) (0.5 g, 2.45 mmol) in 0.2 M sodium hydroxide (50 ml) at 80 °C. After disappearance of the violet color, the separated manganese dioxide was filtered off (Cellite) and extracted with hot 0.02 M NaOH (25 ml). The combined aqueous phases were adjusted to pH 7 with 1 M HCl, the solution was concentrated to 20 ml and acidified with 6 M HCl to pH 2–3. After standing overnight, the crystals were collected and dried *in vacuo*. Yield 262 mg (31%). The crystals decompose above 300 °C. For elemental analysis, 20 mg of the acid 8 in 0.5 ml 0.5 M NaOH was placed over 8 M HCl and the thus obtained crystals of the acid 8 were dried *in vacuo*. For C₁₄H₈N₂O₈·H₂O (350.3) calculated: 48.01% C, 2.88% H, 8.00% N; found: 48.07% C, 2.63% H, 7.88% N. ¹H NMR (200 MHz; DMSO-*d*₆; 50 °C): 9.12 s (2,2',6,6'-H); 13.40 bs (COOH). ¹³C NMR (125 MHz; DMSO-*d*₆; 50 °C): 126.25 s (4,4'-C); 152.44 d (2,2',6,6'-C); 165.76 s (3,3',5,5'-C); 177.79 s (COOH). EI MS, m/z : 332 [M]⁺; 314 [M - H₂O]⁺.

Tetramethyl 4,4'-Bipyridine-3,3',5,5'-tetracarboxylate (9)

Tetraacid 8 (0.534 g, 1.53 mmol) was dissolved in boiling DMF (23 ml). After cooling to 0 °C, an excess of ethereal diazomethane was added with stirring. After standing overnight, DMF was evaporated *in vacuo* and the residue chromatographed on silica gel (20 g) in chloroform-methanol (10 : 1). Crystallization from methanol afforded 377 mg (60%) of the product; m.p. 185–187 °C. For C₁₈H₁₆N₂O₈ (388.3) calculated: 55.67% C, 4.15% H, 7.21% N; found: 55.71% C, 4.20% H, 7.18% N. FAB MS, m/z : 389 [M + H]⁺. FAB HRMS, m/z : for C₁₈H₁₆N₂O₈ + H calculated: 389.0985; found: 389.0952. ¹H NMR (200 MHz; CDCl₃): 3.70 s (CH₃); 9.39 s (2,2',6,6'-H).

4,4'-Bipyridine-3,3',5,5'-tetracarboxamide (**3**)

Tetraester **9** (106.5 mg, 0.325 mmol) was stirred with a solution of ammonia in methanol (10 ml; saturated at 0 °C) at ambient temperature to complete dissolution. After standing for 5 days (TLC monitoring) the reaction mixture was evaporated to dryness and the residue crystallized from water. Yield 76.2 mg (73%); m.p. 345–350 °C (decomp.). For $C_{14}H_{12}N_6O_4 \cdot 3H_2O$ (382.2) calculated: 43.98% C, 4.75% H, 21.98% N; found: 43.94% C, 4.76% H, 21.79% N. 1H NMR (200 MHz; DMSO- d_6): 3.34 bs (H_2O); 7.51 bs (NH_2); 8.16 bs (NH_2); 8.71 s (2,2',6,6'-H). FAB MS, m/z : 329 $[M + H]^+$. FAB HRMS, m/z : for $[C_{14}H_{12}N_6O_4 + H]^+$ calculated: 329.0998; found: 329.0971. Crystals for the X-ray analysis were obtained by slow cooling of hot aqueous solution.

4,4'-Bipyridine-3,3',5,5'-tetracarboxamide–Silver(I) Triflate Complex

A solution of tetraamide **3** (60.6 mg, 0.159 mmol) in water (1 ml) was added to a boiling solution of silver(I) triflate (40.8 mg, 0.159 mmol) dissolved in a minimum amount of water. The formed suspension of the salt was dissolved by slow addition of a minimum amount of hot water. After cooling, the product was collected, washed with water and dried *in vacuo*. Yield 73 mg (76%); m.p. 360 °C (decomp.). For $C_{14}H_{12}N_6O_4 \cdot AgCF_3SO_3 \cdot H_2O$ calculated: 29.86% C, 2.34% H, 13.93% N, 17.88% Ag; found: 29.88% C, 2.28% H, 13.81% N, 17.47% Ag. The thus-obtained crystals were directly used for the X-ray analysis.

Single-Crystal X-Ray Analysis

X-Ray data were collected on a Nonius KappaCCD diffractometer, MoK α radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 150(2) K. The structures were solved by direct methods (SIR92¹²), full-matrix least-squares refinements on F^2 were carried out by using the program SHELXL97¹³. All non-hydrogen atoms were refined anisotropically and converged ($(\Delta/\sigma)_{\max} = 0.002$). The positions of hydrogen atoms of **3** were found on a difference Fourier map, C-bound hydrogens were recalculated in idealized positions (riding model) and temperature factors were assigned $H_{\text{iso}}(H) = 1.2 U_{\text{eq}}(\text{pivot atom})$. All others were refined isotropically without restrictions. The hydrogen atoms in $3 \cdot CF_3SO_3Ag \cdot 3H_2O$ were treated in the same way, except the hydrogens of one water molecule, which is disordered in two positions. Only hydrogens of position with higher occupancy were found and refined as a rigid body group with $H_{\text{iso}}(H) = 1.5 U_{\text{eq}}(O)$. The hydrogen of the second position could not be resolved.

The crystallographic parameters are given in Table I. CCDC 187222 (for **3**) and CCDC 187223 (for $3 \cdot CF_3SO_3Ag \cdot 3H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk), and are also available in the form of standard CIF files as produced by SHELX from the author (I.C.).

TABLE I
Crystallographic parameters

Parameter	3	3 · CF₃SO₃Ag
Formula	C ₁₄ H ₁₂ N ₆ O ₄ · 3(H ₂ O)	C ₁₁ H ₁₂ AgN ₆ O ₄ · CF ₃ O ₃ S · 3(H ₂ O)
<i>M</i>	382.34	639.28
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	11.2450(2)	12.5560(3)
<i>b</i> , Å	10.9120(2)	16.2540(4)
<i>c</i> , Å	14.0170(3)	11.5990(3)
β, °	94.2740(13)	107.9320(17)
<i>Z</i>	4	4
<i>V</i> , Å ³	1 715.18(6)	2 252.19(10)
<i>D_c</i> , g cm ⁻³	1.481	1.885
Dimensions, mm	0.5 × 0.25 × 0.2	0.35 × 0.17 × 0.05
μ, mm ⁻¹	0.121	1.079 ^a
<i>h</i> range	-14, 14	-16, 16
<i>k</i> range	-14, 14	-21, 21
<i>l</i> range	-18, 18	-15, 15
Reflections measured	29 786	37 132
- independent (<i>R</i> _{int})	3 937	5 153
- observed [<i>I</i> > 2σ(<i>I</i>)]	3 395	3 914
Parameters refined	300	382
<i>S</i> value	1.084	1.023
<i>R</i> (<i>F</i>) ^b	0.0379	0.0338
<i>wR</i> ^b	0.0958	0.0789
Δρ _{max} ; Δρ _{min} , e Å ⁻³	0.297; -0.314	0.395; -0.982

^a Absorption correction: $T_{\min} = 0.799$, $T_{\max} = 0.953$, multi-scans (SORTAV¹⁴). ^b $R_{\text{int}} = \Sigma |F_o^2 - F_{o,\text{mean}}^2| / \Sigma F_o^2$, $S = [\Sigma (w(F_o^2 - F_c^2)^2) / (N_{\text{diffrs}} - N_{\text{params}})]^{1/2}$, $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for observed reflections, $wR(F^2) = [\Sigma (w(F_o^2 - F_c^2)^2) / (\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

This work was performed within the framework of the research project K4050111/11 and supported by the Grant Agency of the Czech Republic (grant No. 203/00/0138).

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