Silver(I)-Saccharinato Complexes with 2-(Aminomethyl)pyridine and 2-(2-Aminoethyl)pyridine Ligands: [Ag(sac)(ampy)] and $[Ag_2(sac)_2(\mu\text{-aepy})_2]$

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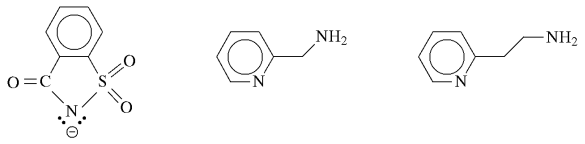
Two new saccharinato-silver(I) (sac) complexes, [Ag(sac)(ampy)] (**1**), and $[Ag_2(sac)_2(\mu\text{-aepy})_2]$ (**2**), [ampy = 2-(aminomethyl)pyridine, aepy = 2-(2-aminoethyl)pyridine], have been prepared and characterized by elemental analysis, IR spectroscopy, thermal analysis and single crystal X-ray diffraction. Complexes **1** and **2** crystallize in the monoclinic space group $P2_1/c$ and triclinic space group $P\bar{1}$, respectively. The silver(I) ions in both complexes **1** and **2** exhibit a distorted T-shaped AgN_3 coordination geometry. **1** consists of individual molecules connected into chains by N-H···O hydrogen bonds. There are two crystallographically distinct dimers in the unit cell of **2** and in each dimer, the aepy ligands act as a bridge between two silver(I) centers, resulting in short argentophilic contacts [Ag1···Ag1 = 3.0199(4) Å and Ag2···Ag2 = 2.9894(4) Å]. Symmetry equivalent dimers of **2** are connected by N-H···O hydrogen bonds into chains, which are further linked by aromatic π(py)···π(py) stacking interactions into sheets.

Key words: Saccharinate, 2-(Aminomethyl)pyridine, 2-(2-Aminoethyl)pyridine, Silver(I), Crystal Structure

Introduction

Saccharin ($C_7H_5NO_3S$; also named *o*-benzosulfimide) is currently the most widely used non-caloric artificial sweetener in the world and commercially available as water-soluble alkali salts [1]. Due to the presence of the imino N, carbonyl and sulfonyl O atoms, saccharin seems to be a potential ligand in coordination chemistry. However, metal complexes of neutral saccharin are not known, but its deprotonated anion, saccharinate (sac), readily coordinates to various metal ions [2 – 4]. A literature search showed that among the metal complexes of sac, silver(I) complexes are very rare, and only two metal complexes, [Ag(sac)] [5] and $[Ag(sac)(PPh_3)_2]$ [6], appeared in this field. Recently, we started a research project and reported a number of new mixed-ligand silver(I)-sac complexes: $Na[Ag(sac)_2]$ [7], $[Ag_2(sac)_2(\mu\text{-hep})]_n$ [8], $[Ag_2(sac)_2(pyet)_2]$ [9], $[Ag_4(sac)_4(pypr)_2]$ [9], $[Ag(sac)(\mu\text{-mpy})]_n$ [10] and $[Ag(\mu\text{-sac})(dmpy)]_n$ [10], $[Ag(sac)(py)]_n$ [11], $[Ag_2(sac)_2(en)(H_2O)]_n$ [12] and



sac ampy aepy

$[Ag_2(sac)_2(dmen)_2]$ [12], [py = pyridine, hep = N-(2-hydroxy ethyl)piperazine, pyet = 2-pyridineethanol, pypr = 2-pyridinepropanol, mpy = 2-pyridinemethanol, dmpy = 2,6-pyridinedimethanol, en = ethylenediamine, and dmen = N,N-dimethylethylenediamine].

As a continuation of this work, we herein report the synthesis, thermal, spectroscopic and crystal structures of two new silver(I)-sac complexes with aminoalkylpyridine ligands containing both aromatic and aliphatic nitrogen donor atoms, namely 2-(aminomethyl)pyridine (ampy), 2-(2-aminoethyl)pyridine (aepy), namely [Ag(sac)(ampy)] (**1**), and $[Ag_2(sac)_2(\mu\text{-aepy})_2]$ (**2**).

Results and Discussion

Synthesis

The reaction of sodium saccharinate with $AgNO_3$ in the presence of ampy or aepy at room temperature resulted in the formation of the title complexes, 2-(aminomethyl)pyridinesaccharinatosilver(I) (**1**) and bis{2-(2-aminoethyl)pyridine}-bis(saccharinato) disilver(I) (**2**). Both complexes were obtained in yields over 85%. The analytical data (C, H, N and S) are consistent with the expected formulations of these complexes. The title complexes are non-hygroscopic and stable in air at room temperature. Both complexes are slightly soluble in water and methanol. They do not melt, but decompose at 171 °C and 70 °C, respectively.

Description of the crystal structures

Fig. 1 shows a perspective view of the molecular structure of **1** with atom labelling. Selected interatomic distances and angles are listed in Table 1, together with the hydrogen bonding geometry. The complex crystallizes in the monoclinic space group $P2_1/c$. The silver(I) ion is coordinated by an ampy ligand and a sac ligand, forming a distorted T-shaped AgN_3 motif with an N-Ag-N angle of 160.2(3)°. The ampy ligand behaves as a bidentate N,N' donor chelating ligand, forming a five-membered chelate ring, while sac is N-coordinated. The bite angle of the ampy ligand is 74.1(3)° and significantly contributes to the distortion of the coordination geometry around the silver(I) ion.

Since the ampy behaves as chelating ligand and has a small bite angle, the approach of the pyridine moiety to the silver(I) centre becomes difficult and therefore, the Ag-N_{py} distance of 2.361(8) Å is significantly longer than the Ag-N_{amino} bond distance of 2.196 (6) Å. The Ag-N_{sac} bond distance of 2.107(7) Å is very similar to those reported for several silver(I)-sac complexes [5, 7 – 12], but significantly shorter than the distance of 2.285(8) Å found in $[Ag(sac)(PPh_3)_2]$ [6].

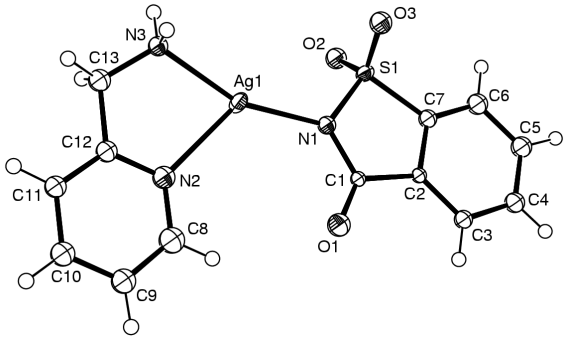


Fig. 1. Molecular structure of **1** showing 50% displacement ellipsoids (arbitrary spheres for the H atoms).

Table 1. Selected bond lengths and angles, and hydrogen bonding geometry of **1**[a].

Bond lengths (Å) and angles (°)			
Ag1-N1	2.107 (7)	N1-Ag1-N3	160.2 (3)
Ag1-N2	2.361 (8)	N1-Ag1-N2	124.6 (3)
Ag1-N3	2.196 (6)	N3-Ag1-N2	74.1 (3)

Hydrogen bonds				
D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N3-H1···O1^{i}	0.92	2.41	3.119 (10)	134
N3-H2···O1^{ii}	0.92	2.13	2.997 (9)	157
C4-H4···O3^{iii}	0.95	2.51	3.268 (12)	137

[a] Symmetry operations: ^{i} $-x$, $1/2+y$, $1/2-z$; ^{ii} x, $1+y$, z; ^{iii} x, $y-1$, z.

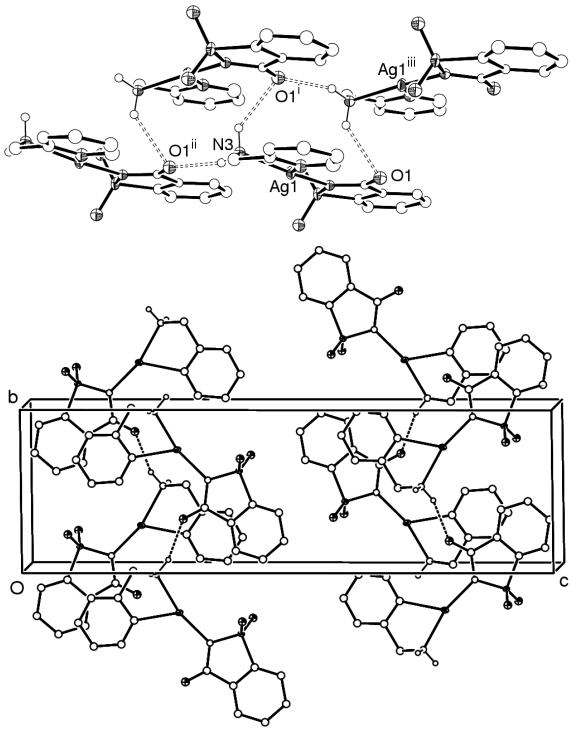


Fig. 2. Top: A fragment of the one-dimensional hydrogen bonded chain arising from N-H···O hydrogen bonds in **1**. Hydrogen bonds are indicated by dashed lines. All C-H hydrogen atoms are omitted for clarity. Symmetry codes ^{i} $-x$, $1/2+y$, $1/2-z$; ^{ii} x, $y+1$, z; ^{iii} $-x$, $1/2-y$, $1/2-z$. Bottom: Packing diagram of **1** viewed along the *a* axis.

Both the pyridine and saccharinate rings are essentially planar and Ag1 is displaced from the best planes of sac and py by −0.113(7) and −0.19(2) Å, respectively. Furthermore, the amine N atom (N3) deviates

Table 2. Selected bond lengths and angles, and the hydrogen bonding geometry of **2**[a].

Bond lengths (Å) and angles (°)			
Ag1-N1	2.449 (2)	N2-Ag1-N3^{i}	160.36 (9)
Ag1-N2	2.209 (2)	N1-Ag1-N2	92.80 (8)
Ag1-N3^{i}	2.194 (2)	N1-Ag1-N3^{i}	104.47 (8)
Ag1···Ag1^{i}	3.0199 (4)	N5-Ag2-N6^{ii}	164.66 (9)
Ag2-N4	2.495 (2)	N4-Ag2-N5	94.21 (8)
Ag2-N5	2.209 (2)	N4-Ag2-N6^{ii}	99.41 (8)
Ag2-N6^{ii}	2.190 (2)		
Ag2···Ag2^{ii,b}	2.9894 (4)		

Hydrogen bonds				
D-H··· A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N3-H2···O1	0.92	2.23	3.012 (3)	142
N6-H5···O6	0.92	2.30	3.076 (3)	142
N3-H1···O1^{iii}	0.92	2.09	2.970 (3)	161
N6-H16···O6^{iv}	0.92	2.12	3.039 (3)	173
C8-H7···O2	0.95	2.57	3.471 (4)	159
C13-H12···O4	0.99	2.49	3.454 (3)	163
C6-H6···O5^{v}	0.95	2.53	3.390 (3)	151
C11-H10···O6^{vi}	0.95	2.48	3.199 (3)	133
C14-H14···O3^{i}	0.99	2.60	3.476 (4)	148
C20-H20···O4^{vii}	0.95	2.40	3.261 (4)	151
C24-H23···O1^{vii}	0.95	2.38	3.264 (4)	155

[a] Symmetry operations: [i] $1-x, 1-y, 1-z$; [ii] $2-x, 2-y, 2-z$; [iii] $-x, 1-y, 1-z$; [iv] $3-x, 2-y, 2-z$; [v] $x-1, y-1, z$; [vi] $x-1, y, z$; [vii] $1+x, y, z$; [b] Ag2 belongs to the second dimer in the asymmetric unit.

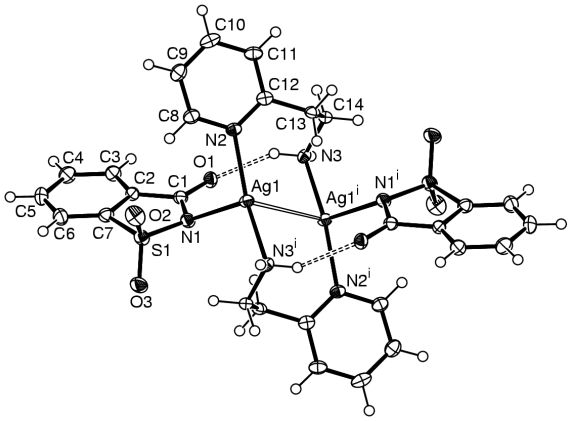


Fig. 3. Dimeric structure of **2** with 50% displacement ellipsoids (arbitrary spheres for the H atoms). The second molecule in the asymmetric unit of **2** was omitted for clarity. Intramolecular hydrogen bonds are indicated by dashed lines. Symmetry code (i) $1-x, 1-y, 1-z$.

from the pyridine ring by $-0.54(2)$ Å. The sac and ampy ligands are almost coplanar and the dihedral angle between them is only $5.76(12)^{\circ}$. The NH_2 hydrogen atoms of the ampy ligand participate in intermolecular hydrogen bonding with the carbonyl oxygen atoms of the sac ligands in the adjacent molecules forming

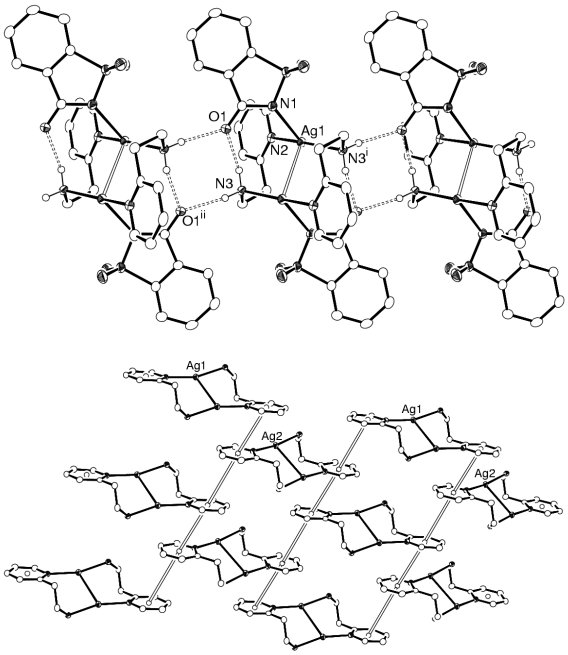


Fig. 4. Top: Interaction of the dimers by N-H···O hydrogen bonds in **2**. Hydrogen bonds are indicated by dashed lines. All C-H hydrogen atoms are omitted for clarity. Symmetry codes [i] $1-x, 1-y, 1-z$; [ii] $-x, 1-y, 1-z$. Bottom: $\pi\cdots\pi$ stacking $(0,-1,1)$ sheets of the [Ag(aepy)] entities. The sac moieties are omitted for clarity.

one-dimensional chains as shown in Fig. 2. The chains are additionally reinforced by C-H···O interactions.

The molecular structure of **2** with the atom labelling is shown in Fig. 3. The selected bond lengths and angles together with hydrogen bonding geometry are collected in Table 2. The complex crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **2** contains two dimeric molecules, in which each silver(I) centre is three-coordinated by an *N*-bonded sac ligand, and two bidentate bridging aepy ligands, exhibiting a distorted T-shaped AgN_3 coordination environment.

The Ag-N_{sac} bond distances of 2.449(2) and 2.495(2) Å are much longer than those reported for other silver(I)-sac complexes [5–12]. The Ag-$N_{py-amino}$ bond distances are practically identical and also similar to corresponding values observed in $[Ag_2(\mu\text{-}NO_3)_2(\mu\text{-aepy})_2]_n$ [13]. The Ag···Ag separations in the dimeric units are 3.0199(4) (Ag1) and 2.9894(4) Å (Ag2), which are significantly shorter than the van der Waals' radius sum for silver(I) (3.44 Å), showing a noticeable interaction between the silver(I) ions. Similar Ag···Ag distances reported

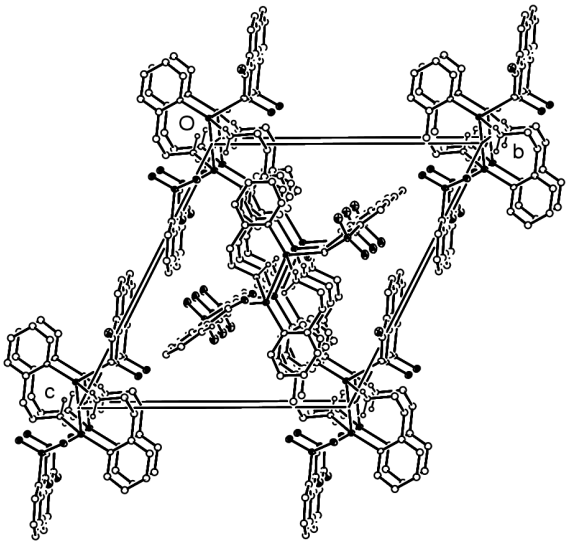


Fig. 5. Packing diagram of **2** viewed along the *a* axis.

for $[Ag_4(sac)_4(pypr)_2]$ [9], $[Ag(sac)(py)]_n$ [11] and $[Ag_2(\mu\text{-}NO_3)_2(\mu\text{-aepy})_2]_n$ [13]. The significance of relatively short Ag-Ag distances has been a subject of discussions. Jansen [14] reported a value of 3.30 Å as the upper limit for an Ag···Ag contact in coordination compounds of silver(I), whereas Dance *et al.* [15] argued that since the linear geometry at silver(I) indicates the fulfilment of its coordination requirements, there is no bonding interaction between silver(I) centres as close to each other as 2.886 Å in $[Ag(SCMeEt)_2]_n$.

The sac and ampy ligands are both essentially planar. Atoms Ag1 and Ag2 are displaced by 1.178(2) and −1.619(2) Å from the corresponding saccharinate planes. Atoms C14-N3 and C28-N6 significantly deviate from the best plane of the pyridine ring. The dihedral angles between the sac and py rings in the two dimeric units with Ag1 and Ag2 are 55.35(10) and 70.43(8)°, respectively, showing the noticeable difference in the conformation of the dimeric forms in the unit cell. Symmetry equivalent dimers are connected by N-H···O hydrogen bonds into chains, which are further linked by aromatic π(py)···π(py) stacking interactions [$C_g\cdots C_g{}^{i} = 3.268$ Å; (i) *x*, *y*, *z*, and $C_g\cdots C_g{}^{ii} = 3.751$ Å; (ii) $x-1$, *y*, *z*] into sheets (see Figs 4 and 5). Additionally, a number of non-classical C-H···O interactions are present.

IR spectra

The assignments of the most characteristic IR bands of the complexes **1** and **2** are given in Table 3. The

Table 3. Selected IR spectral data[a] for **1** and **2**.

Assignments	**1**	**2**
$\nu(NH_2)$	3323, 3249s,br	3357, 3263s,br
$\nu(CH)_{aromatic}$	3093w, 3062w	3074, 3022w
$\nu(CH)_{aliphatic}$	2941w, 2877w	2927w, 2850w
ν(CO)	1651vs, 1630vs	1653vs, 1626vs
ν(CC)	1587s	1583s
ν(CC)	1458m	1458m
ν_s(CNS)	1333m	1334m
$\nu_{as}(SO_2)$	1286sh, 1257vs	1271vs, 1250vs
$\nu_s(SO_2)$	1153vs	1155vs
ν_{as}(CNS)	968s	970s

[a] Frequencies in cm^{-1}. b = broad; w = weak; vs = very strong; s = strong; m = medium; sh = shoulder.

strong and broad absorption bands in the frequency range 3255 – 3357 cm^{-1} correspond to the ν(NH) vibrations of the ampy and aepy ligands. The weak bands around 3070 cm^{-1} are characteristic of the ν(CH) vibrations of the aromatic phenyl and pyridine rings. The stretching vibrations of the carbonyl groups of the title complexes appear as two strong absorption bands at around 1650 and 1630 cm^{-1}. The bands with strong intensity at around 1587 and 1458 cm^{-1} are assigned to the ν(CC) vibrations of the aromatic rings. The asymmetric and symmetric absorption frequencies of the CNS moiety of the saccharinate ligand in **1** and **2** are observed 968 – 1333 and 970 – 1335 cm^{-1}, respectively. The $\nu_{as}(SO_2)$ and the $\nu_s(SO_2)$ modes of sac occur as very strong bands at 1257 – 1153 cm^{-1} for **1**, and at 1250 – 1155 cm^{-1} for **2**.

Thermal analysis of complexes

The thermal decomposition processes for the title complexes were followed up to 800 °C in a static atmosphere of air. Thermal analysis curves of both complexes were recorded using samples mixed with α-Al_2O_3, since we observed that silver forms an alloy with platinum at high temperatures, thus damaging the crucibles.

Complex **1** begins to decompose at 171 °C. The first endothermic DTA peak at 191 °C corresponds to elimination of a NH_3 group (mass loss: found 4.3%, calcd. 4.4%). In a separate experiment, the removal of NH_3 was tested from the evolved gas by using a wet litmus paper. The TG curve shows that the rest of the complex undergoes a continuous mass loss. The exothermic DTA peak at 205 °C may be attributed to the decomposition of the rest of the ampy ligand. A highly exothermic peak at 478 C characterizes the decomposition of sac ligands in air [7 – 10]. The decomposition

Table 4. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_{12}N_3O_3SAg$	$C_{28}H_{28}N_6O_6S_2Ag_2$
M_r	398.19	824.42
T [K]	120 (2)	120(2)
Radiation, λ [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a [Å]	6.6673 (5)	7.9099 (3)
b [Å]	7.9681 (5)	15.0837 (4)
c [Å]	26.287 (2)	15.9151 (5)
α [°]	90.00	114.2820 (17)
β [°]	95.453 (4)	98.8577 (15)
γ [°]	90.00	102.4793 (17)
V [Å^3]	1390.20 (17)	1625.83 (9)
Z	4	2
D_c [g/cm^3]	1.902	1.684
μ mm^{-1}	1.613	1.382
$F(000)$	792	824
Crystal size [mm^3]	$0.24 \times 0.10 \times 0.04$	$0.12 \times 0.09 \times 0.02$
θ Range [°]	4.89/27.80	2.92/27.54
Index range (h,k,l)	$-8/8, -10/10, -34/27$	$-10/10, -19/19, -20/20$
Reflections collected	9423	33500
Independent reflections (R_{int})	7288 (0.0852)	7467 (0.0464)
Absorption correction	multi-scan	multi-scan
Min. and max. transmission	0.698 and 0.938	0.852 and 0.973
Data / parameters	9423 / 96	7467 / 397
Goodness-of-fit on F^2	1.157	1.062
Final R indices $[I > 2\sigma(I)]$	0.0894	0.0328
$wR2$	0.2598	0.0838
Largest diff. peak and hole [e·Å^{-3}]	2.490 and -1.875	0.999 and -0.791

of **1** is complete at 520 °C and the total experimental mass loss value of 73.0% agrees well with the calculated value 72.9%, assuming that the remaining solid residue is metallic Ag.

Complex **2** follows a decomposition path similar to that of **1**. The fist step between 70 and 94 °C with an endothermic DTA peak at 77 °C is attributed to the elimination of NH_3 group (mass loss: found 4.0%, calcd.4.1%). In the subsequent stages, the degradation of remaining aepy and sac ligands occurs with a continuous mass loss. The DTA curve displays two endothermic peaks at 151 and 212 °C, probably due to the decomposition of the remaining part of the ampy ligands, and an extremely exothermic peak at 484 °C, which is characteristic for the sac ligands to give an end product of metallic Ag (total mass loss: found 73.6%, calcd. 73.8%).

Experimental Section

Materials and measurements

All reagents were commercially available and used without further purification. Elemental analyses (C, H, N and S) were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} by using a JASCO FT/IR-430 spectrophotometer. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere at a heating rate of 10 °C min^{-1}.

Synthesis of the silver(I) complexes

Na(sac)·$2H_2O$ (1 mmol, 0.241 g) dissolved in 5 ml distilled water was mixed with $AgNO_3$ (0.17 g, 1 mmol) dissolved in a mixture of water and 2-propanol (20 ml, 1:3) with stirring. The solution immediately became milky. The addition of ampy (0.108 g, 1 mmol) to the milky suspension resulted in a clear solution. The resulting solution was stirred for 30 min at room temperature and was allowed to stand in darkness at room temperature. Colorless crystals of **1** were obtained after a week. Yield 85%. $C_{13}H_{12}N_3SO_3Ag$ (398.19): calcd. C 39.21, H 3.04, N 10.55, S 8.04; found C 39.23, H 3.09, N 10.49, S 7.98.

The preparation method of **2** was the same as described for **1** with aepy replacing ampy. Colorless crystals suitable for X-ray were formed by slow evaporation of the resulting solution in darkness at room temperature after a few days. Yield 87%. $C_{28}H_{28}N_6O_6S_2Ag_2$ (824.42): calcd. C 40.79,

H 3.42, N 10.19, S 7.76; found C 40.73, H 3.49, N 10.10, S 7.83.

X-ray crystallography

Intensity data for the complexes **1** and **2** were collected using a Nonius Kappa-CCD diffractometer. The structures were solved and refined using SHELXS-97 and SHELXL-97 [16]. The crystal quality of **1** was poor and the crystals were twinned. Although only anisotropic refinement on Ag and S was carried out, satisfactory results were obtained. For complex **2**, all non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. The mathematical removal of the effects of a severely disordered, unidentifiable, solvent molecule in **2** was performed by using the program SQUEEZE incorporated in PLATON [17, 18]. All hydrogen atoms in **1** and **2** were included using a riding model. The details of data collection, refinement and crystallographic data are summarized in Table 4.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-269918 (**1**) and CCDC-269919 (**2**). Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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