Synthesis and Characterization of Silver(I) Saccharinate Complexes with Pyrazole and Imidazole Ligands: $[Ag(sac)(pz)(H_2O)]_n$ and $[Ag(sac)(im)] \cdot 2H_2O$

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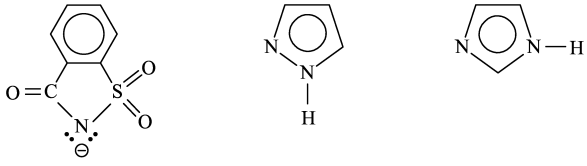
Two new silver(I) saccharinate (sac) complexes, $[Ag(sac)(pz)(H_2O)]_n$ (**1**) and $[Ag(sac)(im)] \cdot 2H_2O$ (**2**) (pz = pyrazole and im = imidazole), have been prepared and characterized by elemental analysis, IR spectroscopy, thermal analysis and single crystal X-ray diffraction. Complexes **1** and **2** crystallize in the monoclinic space group $P2_1/c$ and triclinic space group $P\bar{1}$, respectively. The sac, pz and im ligands all are *N*-coordinated. In **1**, the [Ag(sac)(pz)] units are bridged by aqua ligands to generate a one-dimensional helical chain, in which the silver(I) ions exhibit a distorted square-planar AgN_2O_2 coordination geometry. The polymeric chains are connected by N–H$\cdots$O hydrogen bonds into sheets, which are further linked by aromatic $\pi(\mathrm{pz})\cdots\pi(\mathrm{sac})$ stacking interactions into a three-dimensional supramolecular network. Complex **2** consists of individual molecules containing linearly coordinated silver(I) ions with a slightly distorted coordination of AgN_2. The molecules interact with each other through hydrogen bonds and $\pi\cdots\pi$ interactions to form a three-dimensional supramolecular network.

Key words: Saccharinate, Pyrazole, Imidazole, Silver

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]. Saccharin probably is one of the most studied components of the food ingredients, due to its potential harmfulness and especially its suspected carcinogenic nature [2 – 6]. Although there has been controversy over its safety due to findings of bladder tumors in some male rats fed high doses of saccharin in the past, it is now thought that saccharin is safe at human levels of consumption. On the other hand, the coordination chemistry of saccharin was found to be interesting. The presence of several potential sites such as the imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms makes it a good candidate of a complexing agent in coordination chemistry. However, metal complexes of neutral saccharin are not known, but its deprotonated anion, saccharinate (sac), readily coordinates to various metal ions [7].

Our current interest is to prepare a series of metal–sac complexes with different ligands and we noticed that silver(I) complexes of sac have not received much attention, and only two metal complexes, $[Ag(sac)]_n$ [8] and $[Ag(sac)(PPh_3)_2]$ [9], were reported. As a soft acid, silver(I) coordinates to soft bases such as S- and N-containing ligands and is also known to exhibit flexible coordination geometries such as linear, bent, trigonal planar, T-shaped, tetrahedral and trigonal pyramidal. Recently, we started a research project in this field and reported a number of new monomeric, dimeric, tetrameric and polymeric mixed-ligand silver(I)-sac complexes: $Na[Ag(sac)_2]$ [10], $[Ag_2(sac)_2(\mu\text{–hep})]_n$ [11], $[Ag_2(sac)_2(pyet)_2]$ [12], $[Ag_4(sac)_4(pypr)_2]$ [12], $[Ag(sac)(\mu\text{–mpy})]_n$ [13], $[Ag(\mu\text{–sac})(dmpy)]_n$ [13], $[Ag(sac)(py)]_n$ [14], $[Ag_2(sac)_2(en)(H_2O)]_n$ [15], $[Ag_2(sac)_2(dmen)_2]$ [15], [Ag(sac)(ampy)] [16] and $[Ag_2(sac)_2(\mu\text{-aepy})_2]$ [16], [py = pyridine, hep = *N*-(2-hydroxylethyl)piperazine, pyet = (2-pyridyl)ethanol, pypr = (2-pyridyl)propanol, mpy = (2-pyridyl)methanol, dmpy = 2,6-bis(hydroxymethylpyridine), en = ethylenediamine, dmen = *N*,*N*-dimethylethylenediamine, ampy = 2-(aminomethyl)pyridine and aepy = 2-(2-aminoethyl)pyridine]. As an extension of these studies, we prepared two



sac pz im

new silver-sac complexes, using two heterocyclic five-membered isomers, pyrazole (pz) and imidazole (im). This paper describes the synthesis, spectral, thermal and structural characterizations of a polymeric and a monomeric silver(I) complex of sac, namely $[Ag(sac)(pz)(H_2O)]_n$ (**1**) and $[Ag(sac)(im)] \cdot 2H_2O$ (**2**), respectively.

Results and Discussion

The reaction of sodium saccharinate with $AgNO_3$ in the presence of pz or im at room temperature resulted in the formation of the title complexes, $[Ag(sac)(pz)(H_2O)]_n$ (**1**), and $[Ag(sac)(im)] \cdot 2H_2O$ (**2**). Both complexes were obtained in yields over 87%. Complexes **1** and **2** are non-hygroscopic colorless solids, but they are not light-stable in the solid state and decompose after long exposure to light. Both complexes are soluble in acetonitrile and a warm mixture of water and ethanol. Complexes **1** and **2** do not melt, but decompose at 65 and 43 °C, respectively.

Description of the crystal structures

Fig. 1 shows a view of the asymmetric unit of the complex **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 $P2_1/c$. Complex

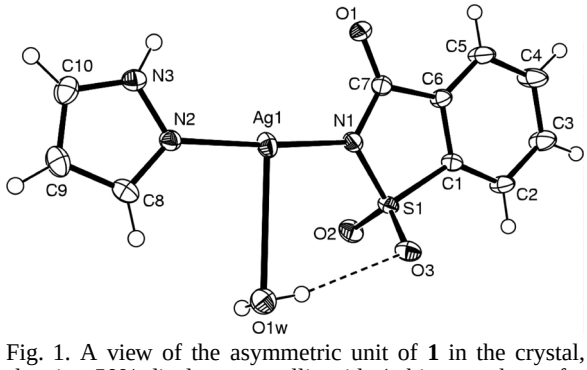


Fig. 1. A view of the asymmetric unit of **1** in the crystal, showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Intramolecular hydrogen bonds are indicated by dashed lines.

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

Bond lengths (Å) and angles (°)			
Ag1–N1	2.094(2)	N1–Ag1–N2	172.60(6)
Ag1–N2	2.096(2)	N1–Ag1–O1W	96.65(5)
Ag1–O1W	3.089(2)	N2–Ag1–O1W	88.10(5)
Ag1–O1W^{i}	3.339(2)	O1W–Ag1–O1W^{i}	166.63(7)
Hydrogen bonds			
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N3–H3a···O1W^{ii}	0.87(3)	2.24(3)	3.051(2)	156(3)
N3–H3a···O1^{iii}	0.87(3)	2.39(3)	2.920 (2)	120(2)
O1W–H1a···O3	0.80(2)	2.44(2)	3.234(2)	169(3)
O1W–H2b···O1^{i}	0.79(3)	2.13(3)	2.917(2)	175(3)

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

1 forms a homopolymer, in which the [Ag(sac)(pz)] units are bridged by aqua ligands to generate a one-dimensional helical chain as shown in Fig. 2. The silver(I) ion is coordinated by a pz ligand and a sac ligand and also by two symmetry equivalent water O atoms. The bond angles suggest that silver(I) ions in **1** exhibit a distorted square-planar AgN_2O_2 coordination geometry.

The Ag–N bond distances are identical, but much shorter than Ag–O_{water} bond distances. The Ag–N_{sac} bond distance of 2.096(2) Å is also similar to those reported for several silver(I)-sac complexes [4, 10–16], but significantly shorter than the corresponding distances of 2.285(8) and 2.449(2) Å found in $[Ag(sac)(PPh_3)_2]$ [5] and $[Ag_2(sac)_2(\mu\text{-aepy})_2]$ [16], respectively. The Ag–N_{pz} bond distance of 2.094(2) Å is very similar to those found for other silver(I) complexes containing pyrazole-type ligands [17]. The bridging link in the chain polymer is provided by two relatively weak Ag–O_{water} bonds, falling in the range from 3.089(2) to 3.339(2) Å. These bond distances are significantly longer than a normal Ag–O_{water} bond distance (2.30–2.60 Å) and suggest very weak Ag···O_{water} interactions. However, these weak Ag–O_{water} interactions maintain the chain structure in **1**. The shortest intra-chain Ag–Ag distance is 6.286 Å. Both sac amd pz rings are essentially planar and the dihedral angle between the best planes of these rings are 12.36(11)°. The individual chains running parallel to the *c* axis are connected head-to-tail through the N–H···O hydrogen bonds to form a two-dimensional layer as illustrated in Fig. 2, and these layers are further linked by aromatic π(pz)···π(sac) stacking interactions $[C_g \cdots C_g{}^{i} = 3.797(1)$ Å; $i = 1-x, 1-y, 1-z]$ into a three-dimensional supramolecular network (see Fig. 2).

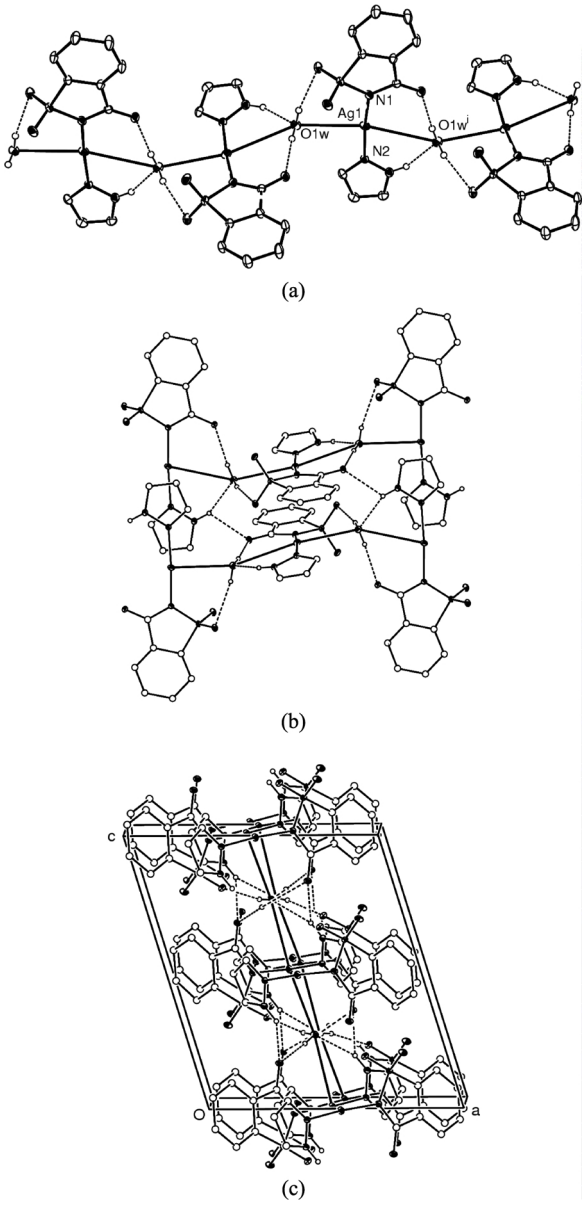


Fig. 2. Top: A fragment of the one-dimensional helical chain arising from Ag–OW–Ag bonds in **1**. Symmetry code (i) = x, $1/2-y$, $z+1/2$. Middle: Interaction of the chains *via* N–H···O hydrogen bonds in **1**, generating a two-dimensional framework. Bottom: Packing diagram of **1** viewed along the *b* axis.

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 silver(I) ion is coordinated by an im ligand and a sac ligand, forming a slightly distorted linear AgN_2 motif with an N–Ag–N angle of

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

Bond lengths (Å) and angles (°)			
Ag1–N1	2.099(1)	N1–Ag1–N2	177.99(6)
Ag1–N2	2.086(1)		

Hydrogen bonds

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N3–H3aO1W^{i}	0.86	1.90	2.755(2)	173
O1W–H1a···O3	0.81(3)	2.21(3)	2.9027(19)	143(3)
O1W–H1b···O2W	0.81(3)	1.97(3)	2.777(2)	170(3)
O2W–H2a···O1^{ii}	0.87(3)	1.96(3)	2.826(2)	177(3)
O2W–H2b···O1^{iii}	0.85(3)	1.95(3)	2.801(2)	174(3)

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

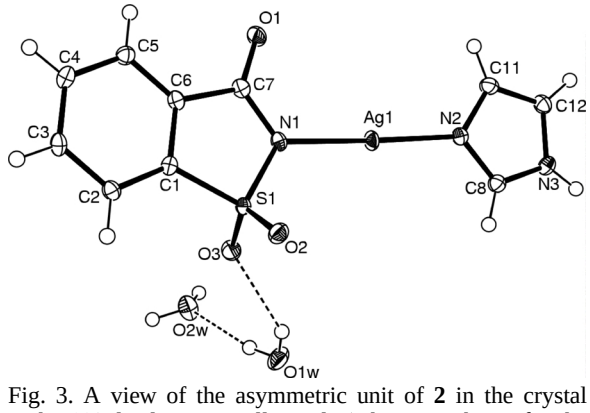


Fig. 3. A view of the asymmetric unit of **2** in the crystal with 50% displacement ellipsoids (arbitrary spheres for the H atoms). Intermolecular hydrogen bonds are indicated by dashed lines.

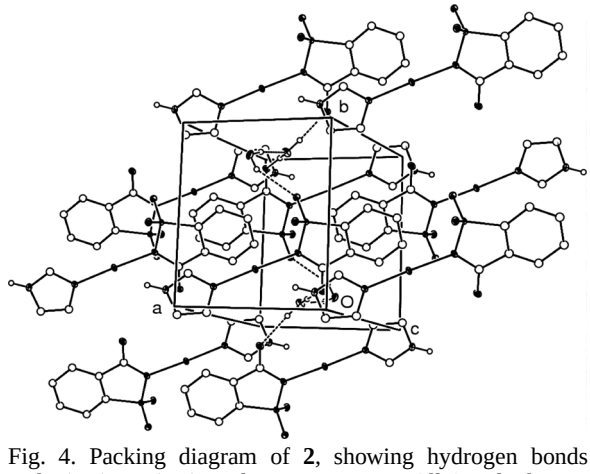


Fig. 4. Packing diagram of **2**, showing hydrogen bonds and π(sac)···π(sac) stacking interactions. All C–H hydrogen atoms are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

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

Assignments	**1**	**2**
υ(OH)	3348s,br	3411-3313s,br
$\upsilon(NH_2)$	3251s,br	3259s,br
$\upsilon(CH)_{aromatic}$	3066w	3080vw
$\upsilon(CH)_{aliphatic}$	2914vw	2933vw
υ(CO)	1651vs	1647vs
υ(CC)	1587s	1585s
υ(CC)	1455m	1456m
υ_s(CNS)	1332s	1334m
$\upsilon_{as}(SO_2)$	1288s, 1251vs	1290vs, 1254vs
$\upsilon_s(SO_2)$	1151vs	1149vs
υ_{as}(CNS)	969vs	964s

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

ca. 178°. In contrast to **1**, silver(I) ions show no tendency to coordinate the water molecules. The Ag–N bond distances are similar to those of **1**.

The sac and im ligands are almost co-planar and the dihedral angle between them is only 4.79(11)°. The crystal structure of **2** presents a number of hydrogen bonds of N–H···O and N–H···O types. Water molecules acts as a bridge between individual molecules and the intermolecular interactions are further reinforced by π(sac)···π(sac) stacking interactions [$C_g \cdots C_g{}^i = 3.741(1)$ Å; $i = -x,\ 1-y,\ 1-z$], leading to a three-dimensional network as shown in Fig. 4.

IR spectra

Selected FTIR data of both complexes are presented in Table 3. The IR spectra of complexes **1** and **2** are almost identical. The bands above 3300 cm^{-1} are attributed to the ν(O–H) vibration of the hydrogen-bonded water molecules. The IR spectra show characteristic bands of the pz and im ligands, ν(N–H) at 3251 and 3259 cm^{-1}, respectively and their ν(C=N) and ν(C=C) bands were overlapped with the sharp carbonyl band of the sac ligand at around 1650 cm^{-1}. Very strong bands at *ca*. 1290 – 1250 and 1150 cm^{-1} characterize the asymmetric and symmetric absorption frequencies of the sulfonyl group in the sac ligand, respectively.

Thermal analysis

The thermal decomposition processes for complexes **1** and **2** 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** dehydrates between 65 and 102 °C (mass loss: found 4.85%, calcd. 4.79%). The endothermic elimination of the pz ligand takes place in the range 106 – 214 °C. The experimental mass loss of 17.86% for this stage agrees well with the calculated mass loss of 18.08%. Two highly exothermic peaks at 313 and 510 °C characterize the decomposition of sac ligands in air (mass loss: found 48.35%, calcd. 48.50%). The decomposition of **1** is complete at 565 °C and the total experimental mass loss value of 71.06% agrees well with the calculated value 71.93%, assuming that the remaining solid residue is metallic Ag.

Complex **2** dehydrates between 43 and 96 °C with two endothermic DTA peaks at 47 and 70 °C (mass loss: found 8.86%, calcd. 9.13%). In the subsequent stages, the degradation of remaining im and sac ligands occurs with a continuous mass loss. The DTA curve displays an endothermic peak at 185 °C, probably due to the removal of the im ligand and two extremely exothermic peaks at 299 and 484 °C are characteristic for the degradation sac ligands to give an end product of metallic Ag (total mass loss: found 72.15%, calcd. 72.62%).

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) · $2H_2O$ (0.24 g, 1 mmol) dissolved in distilled water (5 ml) 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 and then, a white precipitate formed. The precipitate was dissolved in acetonitrile and pyrazole (0.07 g, 1 mmol) was added to the resulting solution. The final solution was allowed to stand in darkness at room temperature. Colorless prism-shaped crystals were obtained within two days. Yield 87%. – $C_{10}H_{10}N_3O_4SAg$ (376.14): calcd. C 31.94, H 2.68, N 11.17, S 8.53; found C 31.72, H 2.79, N 11.39, S 8.48.

The preparation method for **2** was the same as described for **1** with imidazole replacing pyrazole. Colorless prisms

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

	1	**2**
Empirical formula	$C_{10}H_{10}N_3O_4SAg$	$C_{10}H_{12}N_3O_5SAg$
M_r	376.14	394.16
T [K]	100 (2)	100 (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]	11.2240(6)	7.6617(7)
b [Å]	9.2812(5)	8.6844(7)
c [Å]	12.4943(7)	9.9958(9)
α [°]	90	82.664(7)
β [°]	107.190(4)	83.363(7)
γ [°]	90	84.258(7)
V [Å^3]	1243.42(12)	2
Z	4	652.77(10)
D_c [g/cm^3]	2.009	2.005
μ [mm^{-1}]	1.802	1.727
F(000)	744	392
Crystal size [mm^3]	0.56×0.42×0.34	0.56×0.54×0.51
θ Range [°]	2.78/27.82	2.69/27.05
Index range (h, k, l)	−14/14, −12/12, −16/16	−9/9, −11/11, −12/12
Reflections collected	20537	13063
Independent refls (R_{int})	2937 (0.0323)	2840 (0.0334)
Absorption correction	numerical	numerical
Min. and max. transmission	0.474 and 0.623	0.473 and 0.543
Data / parameters	2937 / 185	2840 / 197
Goodness-of-fit on F^2	1.137	1.141
Final R indices [$I > 2\sigma(I)$]	0.0202	0.0178
$wR2$	0.0482	0.0421
Largest diff. peak and hole [e·Å^{-3}]	0.789 and −0.411	0.939 and −0.441

were formed by slow evaporation of the resulting solution in darkness at room temperature after two days. Yield 93%. – $C_{10}H_{12}N_3O_5SAg$ (394.16): calcd. C 30.48, H 3.07, N 10.66, S 8.14; found C 30.62, H 3.22, N 10.50, S 8.33.

X-ray crystallography

The data collection was performed at 100 K for both complexes on a Stoe-IPDS-2 diffractometer equipped with a graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 [18] and refined by a full–matrix least-squares procedure using the program SHELXL-97 [18]. All non-hydrogen atoms were easily found on the difference Fourier map and refined anisotropically. All hydrogen atoms were refined freely, while the NH hydrogen atom of **2** was included using a riding model. Molecular graphics were prepared using ORTEP3 [19]. 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–283303 (**1**) and CCDC-283304 (**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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