



# A novel two-dimensional silver(I) saccharinato coordination polymer constructed from weak Ag···C interactions: Synthesis, IR spectra and X-ray structure

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## ABSTRACT

A new dinuclear silver(I)-saccharinato (sac) complex with acetonitrile (MeCN),  $[\text{Ag}_2(\text{sac})_2(\text{MeCN})_2]_n$  has been synthesized and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The silver(I) ions are doubly bridged by two sac ligands, leading to a short argentophilic contact of 2.9074(3) Å. Each silver(I) ion exhibits a square-planar coordination geometry including the Ag–Ag bonds. The individual dimeric molecules are extended into a two-dimensional layered structure by weak Ag···C<sub>sac</sub> ( $\eta^2$ ) interactions of ca. 3.2 Å. These interactions were discussed and compared with those found in the first silver(I)-sac complex  $[\text{Ag}(\text{sac})]_n$ .

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## 1. Introduction

Saccharin (sacH, 1,1-dioxo-1,2-benzothiazol-3-one) is well-known artificial sweetener and forms a monoanion, saccharinate (sac), when dissolved in water. Due to the presence of the imino N, carbonyl and sulfonyl O atoms, sacH seems to be a potential ligand in coordination chemistry. However, metal complexes of neutral sacH are not known, but sac itself easily coordinates to various metal ions. Metal complexes of sac have received much attention due to their physical and chemical properties [1]. Sac exhibits mono- (N or O), bi- (N, O) or multidentate types of coordination modes and forms metal complexes from mononuclear to coordination polymers. Sometimes, it remains outside the coordination sphere as a counter-ion especially in the presence of relatively bulky ligands.

Over the past decades, the design and synthesis of silver(I) complexes have attracted great attention because of the versatility of their coordination geometries [2–6]. The first silver(I)-sac complex  $[\text{Ag}(\text{sac})]_n$  was reported by Weber, et al. [7]. It is an interesting compound containing tridentate saccharinato ligands and presents an one-dimensional infinite chain structure formed by dimeric

units in which two silver(I) ions are bidentately bridged by two saccharinato anions through the imino N and carbonyl O atoms. The dimeric units are further combined by additional participation of the sulfonyl O atoms, leading to infinite chains. In recent years, we have focused on silver-saccharinate (sac) complexes by reason of the variable coordination modes of sac as well as their interesting structural and solid state properties [8–23].

In this paper, we report on the synthesis, IR spectra and crystal structure characterization of a new silver(I)-sac complex with MeCN (acetonitrile),  $[\text{Ag}_2(\text{sac})_2(\text{MeCN})_2]_n$  (**1**) and present the Ag–C<sub>sac</sub> bonding interactions, for the first time, in a silver(I)-sac complex. Unfortunately, the paper reporting  $[\text{Ag}(\text{sac})]_n$  was hardly descriptive [7] and the interaction of the chains was not taken into consideration. Recently, we have noticed that one-dimensional chains of  $[\text{Ag}(\text{sac})]_n$  interact with each other through Ag–C<sub>sac</sub> bonds. This paper also reports the Ag–C<sub>sac</sub> interactions in  $[\text{Ag}(\text{sac})]_n$  (**2**). Furthermore, the IR spectrum of **1** was discussed by comparing it with those of **2**.

## 2. Results and discussion

### 2.1. Synthesis and IR characterization

Complex **1** was accidentally obtained by the direct reaction of equimolar amount of AgNO<sub>3</sub> and Na(sac) · 2H<sub>2</sub>O in the presence

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**Table 1**  
Selected FTIR spectral data<sup>a</sup> for **1** and **2**.<sup>b</sup>

Assignment	<b>1</b>	<b>2</b>
$\nu(\text{C-H})$	3070w	3087
$\nu\text{C=O}$	1647vs	1640sh, 1612vs
$\nu(\text{CC})$	1583s, 1454m	1577s, 1458sh
$\nu_s(\text{CNS})$	1334m	1338sh
$\nu_{\text{as}}(\text{SO}_2)$	1257vs	1284vs, 1258s
$\nu_s(\text{SO}_2)$	1147vs	1150vs
$\nu_{\text{as}}(\text{CNS})$	960vs	946vs

<sup>a</sup> Frequencies in  $\text{cm}^{-1}$ . b = broad; m = medium; w = weak; vw = very weak; vs = very strong; s = strong; sh = shoulder.

<sup>b</sup> Taken from Ref. [24].

of 2-aminonicotinic acid in a  $\text{H}_2\text{O}/\text{MeCN}$  solution (1/2) at room temperature. In fact, the aim of this study was to synthesize a silver(I)-sac complex with 2-aminonicotinic acid. However, the majority of the yielded crystals was the starting compound  $\text{Na}(\text{sac})$ . The prismatic crystals of **1** were separated and the yield of the reaction was estimated as *ca.* 15%. The attempts for synthesis of this complex using different methods failed. The structural characterization of **1** was performed by FTIR spectrometer and single crystal X-ray measurements.

Selected spectral data for **1** are given in Table 1, together with the data of **2** [24]. As shown in Table 1, the selected spectral data for **1** are consistent with those of **2**. The relatively weak band around  $3070\text{ cm}^{-1}$  is attributed to the absorption of the CH hydrogens. The absorption of the nitrile group appears between  $2200$  and  $2400\text{ cm}^{-1}$  as weak and medium bands, which are expected to be stronger. This may be due to the grinding of the crystals of **1**. The sharp band at  $1647\text{ cm}^{-1}$  is due to the vibration of the carbonyl group of the sac ligand. The carbonyl bands at around  $1650\text{ cm}^{-1}$  usually correspond to only the monodentate coordination of sac via the imino N atom [25]. However, complex **1** contains bridging sac ligands through the carbonyl O atom, and in this case, a significant shift to lower frequencies should be occurred due to a weakening of the carbon–oxygen bond. The spectral analysis shows that no significant shift is observed in the carbonyl band of **1**. It is an unexpected observation and similar findings in the carbonyl band of sac were also observed in the IR spectra of  $[\text{Ag}(\text{sac})(\text{nia})]_n$  [15] and **2** [24]. It may be concluded that the  $\nu(\text{C=O})$  frequency does often not correlate to the right coordination mode of the sac ligand. The symmetric ( $\nu_s$ ) and asymmetric ( $\nu_{\text{as}}$ ) stretching modes of the CNS moiety of the sac ligands appeared at approximately  $1335$  and  $960\text{ cm}^{-1}$ , respectively, while the  $\nu_{\text{as}}$  and  $\nu_s$  stretchings of the  $\text{SO}_2$  group are observed as two strong IR bands centered at  $1257$  and  $1147\text{ cm}^{-1}$ , respectively.

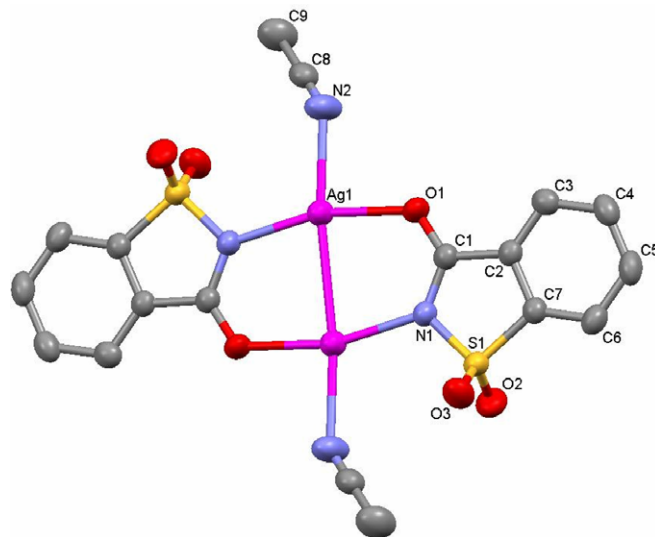
## 2.2. Description of the crystal structure

The title complex crystallizes in the monoclinic space group  $P2_1/c$  and its asymmetric unit contains the half of the compound.

**Table 2**  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for complex **1**.

Ag1–N1	2.172(2)	N1–Ag1–N2	105.21(8)
Ag1–N2	2.380(2)	N1–Ag1–O1	163.22(6)
Ag1–O1	2.212(2)	N2–Ag1–N2	91.55(8)
Ag1–Ag1 <sup>i</sup>	2.9074(3)	N1–Ag1–Ag1 <sup>i</sup>	79.73(5)
		N2–Ag1–Ag1 <sup>i</sup>	170.79(8)
		O1–Ag1–Ag1 <sup>i</sup>	83.79(4)

Symmetry transformations used to generate equivalent atoms: (i)  $= -x + 1, -y + 1, -z$ .

**Fig. 1.** Molecular structure of  $[\text{Ag}_2(\text{sac})_2(\text{MeCN})_2]$  (**1**). H atoms are omitted for clarity.

The selected bond lengths and angles of **1** are listed in Table 2. As shown in Fig. 1, complex **1** has a dinuclear structure in which two silver(I) ions are doubly bridged by two sac ligands via the imino N and the carbonyl O atoms, forming a planar eight-membered bimetallic ring. A MeCN ligand is coordinated to each silver(I) centres as a monodentate ligand through the N atom. Complex **1** exhibits relatively short ligand supported  $\text{Ag} \cdots \text{Ag}$  separations of  $2.9074(3)\text{ \AA}$ , which is smaller than the sum of the van der Waals' radius of two silver(I) ions ( $3.44\text{ \AA}$ ), indicating a noticeable interaction between the silver(I) ions [26]. It has been concluded that this kind of argentophilic interactions results from the  $\text{N-Ag-O}_{\text{carbonyl}}$  angles bigger than *ca.*  $145^\circ$  and becomes stronger as the angle approaches to linearity [27]. When the  $\text{Ag-Ag}$  bonds are taken into consideration, the coordination geometry around each silver(I) ion may be considered as a significantly distorted square plane.

The  $\text{Ag-N}_{\text{sac}}$  bond distance is slightly shorter than the  $\text{Ag-O}_{\text{sac}}$  bond distance and both bond distances are within the normal range observed in the reported silver(I)-sac complexes containing the  $\text{N-O}_{\text{carbonyl}}$  bridged dimers [7,9,10,15]. The relatively long bond length of  $\text{Ag-N}_{\text{MeCN}}$ ,  $2.380(2)\text{ \AA}$ , shows that these MeCN molecules are weakly coordinated to the silver(I) ions and possibly easy to be substituted. Therefore, the rigid dinuclear unit may be a potential building block to construct designed coordination polymers with different dimensionality.

X-ray structural analysis show that there are weak  $\text{Ag} \cdots \text{C}$  ( $\eta^2$ ) interactions between silver(I) ions and benzene rings of the neighboring molecules with the  $\text{Ag-C}$  distances of  $3.166$  and  $3.201\text{ \AA}$ , which are noticeably shorter than to the sum of van der Waals radii of  $\text{Ag(I)}$  ion and the carbon atom ( $3.42\text{ \AA}$ ) (Fig. 2). Complex **1** is the first example displaying an interaction of the phenyl ring of sac with silver(I), since the reported silver(I) complexes in [8–23] did not exhibit such interactions. Some polymeric silver(I) complexes of aromatic ligands have been reported to present similar  $\text{Ag} \cdots \text{C}$  interactions with  $\text{Ag-C}$  bond distances of *ca.*  $2.80$ – $3.38\text{ \AA}$  [28–33]. Therefore, these interactions in **1** may be considered as a weak dihapto aromatic coordination of the benzene ring of sac to the silver(I) ion, and are very important, in the present case, for the packing of **1** in the solid state. As shown in Fig. 3, the dinuclear molecules of **1** are connected by these  $\text{Ag} \cdots \text{C}$  interactions into a two-dimensional layered structure extending along the crystallographic *ac* plane. In this case, the coordination environment around

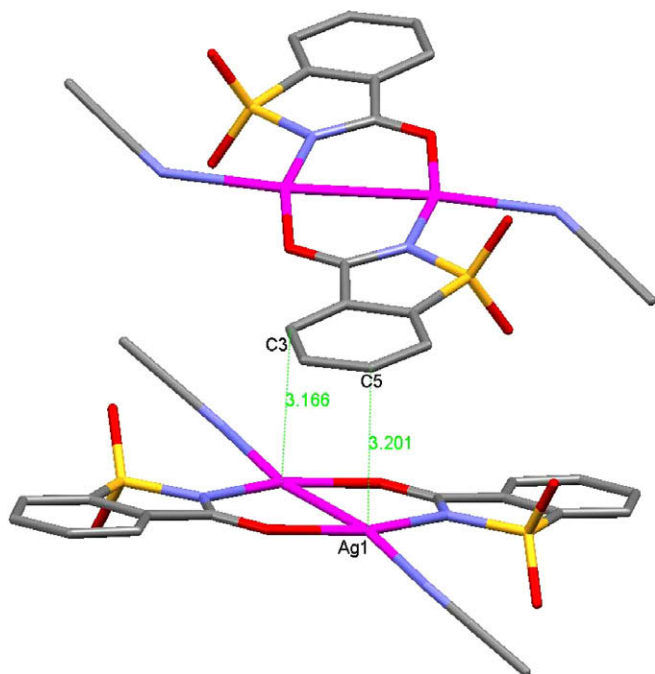


Fig. 2.  $\eta^2$  Ag...C interactions in **1**.

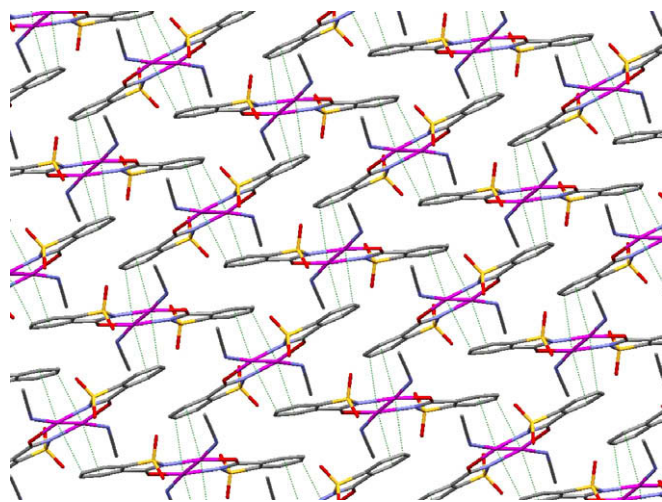


Fig. 3. A part of two-dimensional network of **1**, generated from the Ag...C interactions.

each silver(I) ion in **1** may be considered as a distorted octahedral geometry by including the weak Ag-C bonds.

Our observations showed that such weak Ag...C interactions were also present in the first silver(I)-sac complex  $[\text{Ag}(\text{sac})]_n$  (**2**). The description of the structure of **2** was very short [7] and not included interactions between the one-dimensional polymeric chains of **2**. Fig. 4 shows that each silver(I) ion is involved in weak Ag...C ( $\eta^3$ ) interactions in the range 2.978–3.332 Å with the benzene ring of the sac ligands in the adjacent linear chains. The individual polymeric chains are extended to a two-dimensional sheet by these weak Ag...C interactions (Fig. 5). Compared to complex **1**, one of the Ag-C bonds in **2** are much stronger and the benzene ring coordinates to silver(I) with an  $\eta^3$  mode instead of an  $\eta^2$  mode. The weak Ag...C interactions in both complexes **1** and **2** seem to be highly significant factors in the construction of polymeric networks in the solid state.

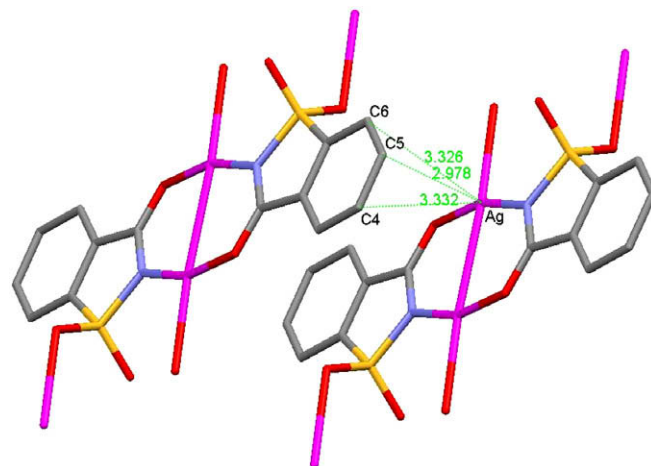


Fig. 4.  $\eta^3$  Ag...C interactions in  $[\text{Ag}(\text{sac})]_n$  (**2**).

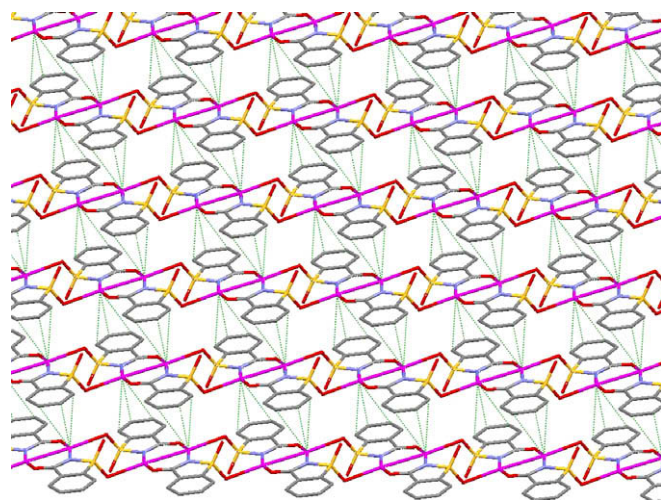


Fig. 5. A fragment of two-dimensional network of **2**, showing interactions between the linear chains via the Ag...C interactions.

### 3. Conclusions

A new dinuclear silver(I)-sac complex with MeCN (**1**) has been synthesized and structurally characterized. In the dimeric structure, the silver(I) ions are bridged by two sac ligands leading to strong argentophilic interactions. Complex **1** is the first example of an extended structure involving Ag...C interactions. The molecules of **1** are assembled into a two-dimensional structure by weak Ag...C interactions between the silver(I) ion and the phenyl ring of sac. Revisiting the structural data of the first silver(I)-sac complex  $[\text{Ag}(\text{sac})]_n$  (**2**) showed that the weak Ag...C interactions are also present in **2** and links the chains into two-dimensional layered structure. The weak Ag...C interactions are observed for the first time in silver(I)-sac complexes and it appears that in the both complexes, the weak Ag...C interactions are a key factor controlling packing of molecules and intermolecular interactions as well as the structure dimensionality.

### 4. Experimental

#### 4.1. Materials and measurements

All reagents were purchased from commercial sources and used without further purification. The elemental analyses (C, H and N)

**Table 3**  
Crystallographic data and structure refinement for complex **1**.

Formula	C <sub>18</sub> H <sub>14</sub> Ag <sub>2</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>
Molecular weight	662.19
Temperature (K)	295(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	
<i>a</i> (Å)	9.4408(6)
<i>b</i> (Å)	11.4978(8)
<i>c</i> (Å)	9.6158(6)
$\beta$ (°)	92.574(5)
Volume (Å <sup>3</sup> )	1042.73(12)
<i>Z</i>	2
Calculated density (g/cm <sup>3</sup> )	2.109
$\mu$ (mm <sup>-1</sup> )	2.124
<i>F</i> (000)	648
Crystal size (mm <sup>3</sup> )	0.54 × 0.49 × 0.30
$\theta$ range (°)	2.76–26.00
Index ranges	–11 ≤ <i>h</i> ≤ 11; –14 ≤ <i>k</i> ≤ 14; –11 ≤ <i>l</i> ≤ 11
Reflections collected	14775
Independent reflections [ <i>R</i> <sub>int</sub> ]	2051 [0.0802]
Reflections observed (>2 $\sigma$ )	1938
Absorption correction	Numerical
Maximum and minimum transmission	0.745 and 0.544
Data/parameters	2051/158
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.187
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0222 <i>wR</i> <sub>2</sub> = 0.0523
Largest difference peak and hole (e Å <sup>-3</sup> )	0.522 and –0.222

were performed on a Vario EL Elemental Analyser. IR spectra were recorded on a Bruker WERTEX 80V FTIR spectrophotometer as KBr pellets in the frequency range 4000–400 cm<sup>-1</sup>.

Complex **1** was prepared by the following method: Na(sac) · 2H<sub>2</sub>O (1 mmol, 0.24 g) was added to the solution (20 ml) of AgNO<sub>3</sub> (1 mmol, 0.17 g) dissolved in the mixture of water and isopropanol (1:3, v:v) with stirring.

#### 4.2. Synthesis of [Ag<sub>2</sub>(sac)<sub>2</sub>(MeCN)<sub>2</sub>]<sub>*n*</sub>

This complex was prepared by the following method: solid Na(sac) · 2H<sub>2</sub>O (1 mmol, 0.24 g) was added to the solution of AgNO<sub>3</sub> (0.17 g, 1 mmol) dissolved in H<sub>2</sub>O/MeCN (1/2) (30 ml). Then, a suspension with a white precipitate formed and the addition of 0.14 g (1 mmol) 2-aminonicotinic acid to the suspension resulted in a clear solution, which was kept in darkness at room temperature. Colorless prismatic crystals of [Ag<sub>2</sub>(sac)<sub>2</sub>(MeCN)<sub>2</sub>]<sub>*n*</sub> (**1**) appeared after two weeks. Yield ~15%. Anal. Calc. for C<sub>18</sub>H<sub>14</sub>Ag<sub>2</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: C, 32.65; H, 2.13; N, 8.46. Found: C, 32.87; H, 2.35; N, 8.68%. IR (KBr): 3081, 1641, 1591, 1462, 1343, 1274, 1155, 1055, 966, 877, 748, 708, 678, 618, 635, 549 cm<sup>-1</sup>.

#### 4.3. X-ray crystallography

The data collection was performed at 295 K on a Stoe-IPDS-2 diffractometer equipped with a graphite monochromated Mo K $\alpha$

radiation ( $\lambda$  = 0.71069 Å). The structures were solved by direct methods using SHELXS97 [34] and refined on *F*<sup>2</sup> by a full-matrix least-squares using SHELXL97 [34]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. All CH hydrogen atoms were included using a riding model. Details of crystal data, data collection, structure solution and refinement are given in Table 3.

#### Supplementary material

CCDC 698450 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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