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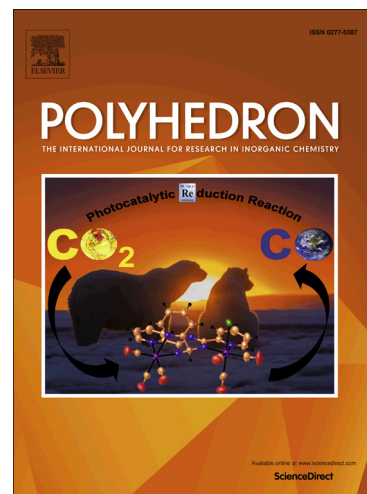
PII: S0277-5387(16)30612-X  
DOI: <http://dx.doi.org/10.1016/j.poly.2016.11.029>  
Reference: POLY 12337

To appear in: *Polyhedron*

Received Date: 26 August 2016  
Revised Date: 8 November 2016  
Accepted Date: 13 November 2016

Please cite this article as: F. Semerci, H. Erer, O. Şahin, Synthesis and characterization of new Ag(I) coordination networks based on saccharinate and bis(isopropylimidazole) ligands exhibiting very close C–H ···Ag interactions, *Polyhedron* (2016), doi: <http://dx.doi.org/10.1016/j.poly.2016.11.029>

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**Synthesis and characterization of new Ag(I) coordination networks  
based on saccharinate and bis(isopropylimidazole) ligands exhibiting very close C–  
H···Ag interactions**

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**Abstract**

Two Ag(I) coordination networks, formulated as  $[\text{Ag}(\text{sac})(\mu\text{-bisopib})]_n$  (**1**) and  $[\text{Ag}(\text{sac})(\mu\text{-bisopix})]\cdot\text{H}_2\text{O}$  (**2**), have been synthesized based on the bis(isopropylimidazole) ligands 1,4-bis(2-isopropyl-1H-imidazol-1-yl)butane (bisopib) and 1,4-bis((2-isopropyl-1H-imidazol-1-yl)methyl)benzene (bisopix), respectively, along with saccharinate (sac) ligands. All the complexes were characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction studies. The X-ray crystallographic studies of **1** and **2** revealed that the Ag(I) ions are  $\mu$ -bridged by the bis(isopropylimidazole) derivative ligands to generate 1D zig-zag polymer and dinuclear structures, respectively. As far as we know, complex **1** shows the closest C-H $\cdots$ Ag interaction distance among similar literature examples. In complex **1** adjacent 1D coordination polymers are further joined by C-H $\cdots$ O hydrogen bonds and  $\pi\cdots\pi$  interactions, generating a 3D supramolecular network. The C-H $\cdots$ O hydrogen bonds and C-H $\cdots\pi$  interactions play a crucial role in the architecture of the 3D network of complex **2**. Thermal decompositions and photoluminescent properties of the Ag(I) complexes are also discussed herein.

**Keywords:** Coordination polymers; Saccharinate complexes; Ag(I) complexes, C-H $\cdots$ Ag interaction

## 1. Introduction

The synthesis of metal organic networks based on transition metals and bis(imidazole) ligands is an important research area, owing to a new type of supramolecular interactions and the potential applications of these products [1-8]. The synthesis of metal organic networks relies on certain factors, such as the nature of the metal ions and the coordination ability of the ligands [9,10]. Hydrogen bonding plays an important role in structural chemistry, catalysis and biologic processes [11-13].

Bis(imidazole) ligands containing aliphatic or aromatic groups are a good option for choosing an N-donor ligand and when they are coordinated by transition metal ions, structural diversity can be observed due to the rotation ability of such flexible ligands [5]. Coordination polymers of flexible bis(imidazole) ligands such as 1,2-, 1,3- and 1,4-bis(imidazol-1-ylmethyl)benzene have been appearing commonly in the literature [14-17]. Saccharin is an artificial sweetener and is chosen because it is a polyfunctional ligand and shows coordination to metal atoms through its imino nitrogen, carbonyl and sulfonyl oxygen atoms, as such its anions may act as bridging ligands in various coordination modes [18-25].

The most controversial hydrogen bond type is the C–H···M weak interaction [26]. During the last decade, new types of hydrogen bonding specific for Ag(I) complexes were found and investigated [27-31]. Ag(I) ions possess d-type paired electrons, so it was assumed that they could behave as acceptors to aliphatic and/or aromatic hydrogen atoms. Research on the usage of C–H···Ag interactions is rare in the coordination chemistry of Ag(I) complexes, whereas C–H···Ag interactions in building new metal organic networks have attracted attention. In this study, to investigate C–H···Ag interactions we used bis(isopropylimidazole) ligands.

Ag(I)-Sac complexes have been synthesized due to their interesting structural properties [23,25,32-45]. To further investigate the influence of the bis(isopropylimidazole) derivative

ligands on the formation of supramolecular architectures of Ag(I)-saccharinate complexes, two bis(isopropylimidazole) containing ligands, flexible 1,4-bis(2-isopropyl-1H-imidazol-1-yl)butane (bisopib) and semi-flexible 1,4-bis((2 isopropyl-1H-imidazol-1 yl)methyl)benzene (pbisopix) (Scheme 1) were chosen as neutral ligands in this work. Bisopib and pbisopix are bidentate ligands with flexible aromatic or aliphatic skeletons which contain methylene groups. When coordinating to metal centers, the different flexibilities and steric effects of these ligands may diversify the topologies of the networks.

In this paper, we describe the syntheses of two new Ag(I)-saccharinate complexes,  $[\text{Ag}(\text{sac})(\mu\text{-bisopib})]_n$  (**1**) and  $[\text{Ag}(\text{sac})(\mu\text{-bisopix})]\cdot\text{H}_2\text{O}$  (**2**). In the complexes, the bis(isopropylimidazole) ligands show the ability to build the complexes and they play an important role in directing the final networks. The crystal structures of these complexes and an investigation of the effect of the sac anions and bis(isopropylimidazole) ligands on the ultimate network is discussed.

## 2. Experimental

### 2.1. Measurements and materials

All starting materials were of analytical reagent grade and used as received without further purification. The bisopix and bisobip ligands were synthesized according to the literature [4]. Elemental analyses for C, H, and N were carried out at the TÜBİTAK Marmara Research Centre. The IR spectra were recorded in the range  $4000\text{-}400\text{ cm}^{-1}$  by means of a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. The photoluminescence (excitation and emission) spectra for the solid sample of the complexes were determined with a Perkin-Elmer LS-55 spectrophotometer using a slit width of 15 nm excitation and 7 nm emissions at room temperature. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record

simultaneous TG, DTG and DTA curves in a static air atmosphere at a heating rate of 10 °C min<sup>-1</sup> in the temperature range 30-700 °C using platinum crucibles.

## 2.2. Crystallographic analyses

Suitable crystals of **1** and **2** were selected for data collection, which was performed on a D8-QUEST diffractometer equipped with graphite-monochromatic Mo-K<sub>α</sub> radiation at 296 K. The structures were solved by direct methods using SHELXS-97 [1] and refined by full-matrix least-squares methods on F<sup>2</sup> using SHELXL-2013 [2]. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of the C5 atom in **1** and O4 and C26 atoms in **2** were located in a difference map refined subject to a DFIX restraint. The other H atoms of C atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93-0.98 Å. Some atoms of the sac ligand in **1** and the pbisopix ligand in **2** are disordered, which results in symmetrical disorder. The refinements of the disorders were made anisotropically using PART and EADP restrictions. These disorders were modelled as two different orientations with occupancy factors of 0.50 and 0.50. The following procedures were implemented in our analysis, data collection: Bruker APEX2 [3]; program used for molecular graphics: MERCURY programs [4]; software used to prepare material for publication: WinGX [5]. Details of the data collection and crystal structure determinations are given in Table 1.

## 2.3. Preparation of the complexes

A mixture of Na(sac)·H<sub>2</sub>O (0.50 g, 2.24 mmol) and AgNO<sub>3</sub> (0.38 g, 2.24 mmol) was stirred in water (20 mL) at 60 °C for 30 min and then bisopib (0.61 g, 2.24 mmol) was added to the mixture. A solution of ammonia was added until the suspension dissolved. The solution was stirred for 60 min and then filtered. The resulting solution was kept in the dark at room

temperature for 2 days to produce colorless crystals of **1**. Yield: 0.859 g, 68% (based on AgNO<sub>3</sub>). Anal. Calc. for C<sub>23</sub>H<sub>30</sub>AgN<sub>5</sub>O<sub>3</sub>S: C, 48.94; H, 5.36; N, 12.41% Found: 49.24; H, 4.88; N, 13.22%. IR (KBr, cm<sup>-1</sup>): 3138(m), 3115(s), 2954(s), 2922(m), 2862(w), 1663(vs), 1591(w), 1491(m), 1456(m), 1327(w), 1285(vs), 1153(s), 1070(m), 958(s), 760(m), 729(w), 679(w), 600(w), 542(w), 449(w)

The synthetic procedure for **2** was similar to that of **1**, except that pbisopix was replaced by bisopib (0.722 g, 2.24 mmol). After three days, colorless crystals of **2** were obtained. Yield: 0.83 g, 59% (based on AgNO<sub>3</sub>). Anal. Calc. for C<sub>27</sub>H<sub>32</sub>AgN<sub>5</sub>O<sub>4</sub>S: C, 51.43; H, 5.12; N, 11.11% Found: C, 51.27; H, 4.98; N, 11.42%. IR (KBr, cm<sup>-1</sup>): 3410(br), 3120(m), 2968(s), 2930(m), 2866(w), 1651(vs), 1587(w), 1516(m), 1490(s), 1456(m), 1365(w), 1340(w), 1269(vs), 1149(vs), 1070(m), 959(s), 750(m), 731(w), 679(w), 602(w), 538(w), 426(w)

### 3. Results and discussion

#### 3.1. Synthesis and spectral characterization

The reaction of bisopib and pbisopix with saccharinate ligands and Ag(I) ions in diluted ammonia solution at room temperature resulted in the crystallization of the silver complexes **1** and **2**. Elemental analysis for complexes **1** and **2** agreed with the formula of the complexes, as confirmed by X-ray single crystal analysis. Moreover, microanalysis data confirmed the 1:1 ratio of silver ions to sac and bisopib or pbisopix ligands in the complexes. Both complexes were obtained as colorless crystals in high yields of over 60%.

The complexes were investigated by FT-IR spectroscopy (Fig. S1.). Selected absorption bands of the complexes are presented in Table 2, together with the FT-IR data of [Ag(sac)] [46] and [Ag<sub>2</sub>(sac)<sub>2</sub>(o-bix)<sub>2</sub>] (o-bix = 1,2-bis(imidazole-1-ylmethyl)benzene) [47]. The absorption band seen in the range 2968-2862 cm<sup>-1</sup> is attributed to the aliphatic ν(C-H) vibration of the C-H groups of the bisopib and pbisopix ligands. The stretching bands of CO,

SO<sub>2</sub> and CNS have been thought as vital bands for the characterization of saccharinate complexes [50]. The strong and sharp bands at 1663 and 1651 cm<sup>-1</sup> are assigned to the carbonyl group of the sac ligand for complexes **1** and **2**, respectively [48]. The strong bands at 1285, 1269 and 1153, 1150 cm<sup>-1</sup> for complexes **1** and **2** correspond to the asymmetric and symmetric stretches of the SO<sub>2</sub> group, respectively. The asymmetric and symmetric absorption bands of the CNS moiety of the sac ligand in all the complexes are observed at 1354 and 1340 cm<sup>-1</sup>, respectively.

Luminescent d<sup>10</sup> metal complexes have been evolving and gaining attention [49-51]. The studies of the photoluminescent properties of Ag(I) complexes reveal that their properties stem from the metal ions and the ligands coordinated with them [28,29,52]. Due to the luminescent properties of Ag(I) complexes, the emission spectra of the complexes and the ligand as NaSac were investigated in the solid state at room temperature (Fig. 1).

NaSac shows a photoluminescent emission band at 339 nm ( $\lambda_{\text{ex}} = 275$  nm) [21] upon excitation at 275 nm, which is attributed to the  $\pi^* \rightarrow \pi$  and/or  $\pi^* \rightarrow n$  transition [38]. Complexes **1** and **2** show luminescence with an emission band maximum at 422 and 422 nm and a shoulder at 484 and 477 nm upon excitation at 347 and 346 nm, respectively. The emissions of the complexes may be attributed to ligand centered luminescence emissions. Similar emission bands at 420 and 487 nm for [Ag(sac)(Ph<sub>2</sub>SNH)] (Ph<sub>2</sub>SNH = S,S-diphenylsulfimide [53] and 427 nm for [Ag<sub>4</sub>(sac)<sub>4</sub>(mpyz)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (mpyz = 2-methylpyrazine) [54] have been recently observed.

### 3.2. Crystal structures

The relevant crystal data and experimental conditions with the final parameters are summarized in Table 2. Details of the interaction distances and geometries are given in Tables 3-5.



### 3.2.1. Crystal structure of [Ag(sac)( $\mu$ -bisopib)] (1)

The molecular structure of **1**, with the atom numbering scheme, is shown in Fig. 2. Selected bond distances and angles are listed in Table 3. The single X-ray single crystal analysis reveals that complex **1** crystallizes in the monoclinic space group C2/c and is a one-dimensional coordination polymer. The asymmetric unit of **1** consists of half an Ag(I) ion, half a bisopib ligand and half a sac ligand. The Ag(I) ion is located on a center of symmetry and is coordinated by two nitrogen [Ag1-N1=2.282(3) Å] atoms from two different bisopib ligands and one nitrogen atom [Ag1-N3=2.164(4) Å] from a sac ligand. The bisopib ligand acts as a bidentate bridging ligand between two Ag(I) centers through the imidazolyl N atoms, forming a one-dimensional zig-zag chain. The sac ligand acts as a monodentate ligand, coordinated by the imino nitrogen atom. The Ag1-N1 bond length (2.282(3) Å) is shorter than the corresponding bond in [and [Ag<sub>2</sub>(sac)<sub>2</sub>( $\mu$ -aepy)] (2.449(2) Å)[55]. However, this bond distance is similar to the corresponding value found in the reported complex [Ag<sub>2</sub>(sac)<sub>2</sub>( $\mu$ -pbix)<sub>2</sub>] (2.172(3) Å) [56]. The coordination sphere of the Ag(I) ion is a trigonal planar coordination geometry. The Ag(I) ions are bridged by bisopib ligands to generate a zig-zag 1D coordination polymer running parallel to the [101] direction (Fig. 3(a)), with an Ag $\cdots$ Ag separation of 12.824 Å. It is worth mentioning that the most important structural property of complex **1** is the presence of very close C-H $\cdots$ Ag(I) interactions between the Ag(I) and H atoms of the isopropyl groups of the bisopib ligands, as characterized by the single crystal X-ray studies (Fig. 3(a)). As far as we know, complex **1** shows the closest C-H $\cdots$ Ag(I) interaction distance among similar literature examples (Table 4). The parameters of the C-H $\cdots$ Ag(I) interaction between the Ag(I) ion and H atom of the bisopib ligand (Fig. 2) are: Ag1 $\cdots$ H5A 2.63(7) Å; Ag1 $\cdots$ C5, 3.427(8) Å; C5-H5A $\cdots$ Ag1, 143.1(2) $^\circ$ . Complex **1** also contains one  $\pi\cdots\pi$  interaction. An intermolecular  $\pi\cdots\pi$  contact occurs between imidazole rings of neighboring molecules. The distance between the ring centroids is 3.75 Å. Adjacent 1D

coordination polymers are further joined by C-H $\cdots$ O hydrogen bonds and  $\pi\cdots\pi$  interactions, generating a 3D supramolecular network (Fig. 3(b) and Table 5).

### 3.2.2. Crystal Structure of [Ag(sac)( $\mu$ -bisopix)] $\cdot$ H<sub>2</sub>O (**2**)

The asymmetric unit of **2** consists of one Ag(I) ion, one bisopix ligand, one sac ligand and a non-coordinated water molecule (Fig. 4). The Ag(I) ion is coordination by two nitrogen [Ag1-N2A = 2.254(14) Å and Ag1-N5<sup>i</sup> = 2.184(4) Å] atoms from two different bisopix ligands and one nitrogen atom [Ag1-N1 = 2.291(4) Å] from the sac ligand, thus showing a trigonal planar coordination geometry [(i) -x+1, -y+1, -z] (Table 3). The Ag(I) ions are bridged by bisopix ligands to generate an [Ag<sub>2</sub>(bisopix)<sub>2</sub>(sac)<sub>2</sub>] cluster, with an Ag $\cdots$ Ag separation of 10.295 Å. Like complex **1**, complex **2** shows a C-H $\cdots$ Ag(I) close interaction (Fig. 4 and Table 4), [Ag1 $\cdots$ H26D = 2.74(8) Å, Ag1 $\cdots$ C26 = 3.494(8) Å and C26-H26A $\cdots$ Ag1 = 138.4(5) $^\circ$ ] and C-H $\cdots$  $\pi$  interactions. The C-H $\cdots$  $\pi$  interactions occur between the bisopix and sac ligands. Details of these interactions are presented in Table 3. The [Ag<sub>2</sub>(bisopix)<sub>2</sub>(sac)<sub>2</sub>] clusters are joined by C-H $\cdots$  $\pi$  interactions, generating a 2D network (Fig. 4). The C-H $\cdots$ O hydrogen bonds and C-H $\cdots$  $\pi$  interactions play a crucial role in the architecture of the 3D network (Fig. 5. and Table 5).

### 3.3 Structural comparison

Within the scope of this study, bis(imidazole) derivatives ligands containing isopropyl groups were preferred to examine C-H $\cdots$ Ag interactions. In addition, the carbon skeletons of the ligands including isopropyl groups at the ends were selected considering them as flexible and semi-flexible. The reason for this choice was to examine the effect of the flexibility of these groups on the final supramolecular structure. Complex **1**, containing the bisopib ligand with a flexible aliphatic -(CH<sub>2</sub>)<sub>4</sub>- carbon skeleton, exhibited a 1D zig-zag structure. In addition, very close C-H $\cdots$ Ag interactions were observed in complex **1**. Complex **2** has the bisopix ligand,

which has a semi-flexible xylene carbon skeleton. Complex **2** has a dinuclear structure because the semi-flexible groups do not rotate enough to form polynuclear complexes.

### 3.4. Thermal analysis

To study the thermal stabilities of the synthesized complexes, thermal analyses (TG, DTG and DTA) were performed on the as-synthesized single crystal samples (Fig. S2 and S3.). [Ag(sac)( $\mu$ -bisopib)] (**1**) melts at 201 °C and begins to decompose at 213 °C. The thermal decomposition of **1** occurs in two steps. It is hard to understand the decomposition steps owing to a continuous mass loss, as seen in the TG curve of **1**. The weight loss of 81.17% in the region 213-622 °C corresponds to the elimination of one bisopib and one sac ligand for **1** (calculated: 80.88% and  $DTG_{max.} = 360.60$  and  $592.42$  °C for **1**). Final product for **1** was calculated as metallic silver [57].

The first stage between 106 and 116 °C for [Ag(sac)( $\mu$ -bisopix)]·H<sub>2</sub>O (**2**) corresponds to the endothermic elimination of one water molecule, with an experimental mass loss of 3.67% (calcd. mass loss 2.85%). The second stage, between 116 and 332 °C, is related to elimination of one bisopix ligand ( $DTG_{max.} = 346.45$  °C, found 51.54%, calcd. 51.14%). The last stage, between 322 and 440 °C, is related to the decomposition of the sac ligand, with an exothermic effect ( $DTG_{max.} = 551$  °C, found 26.25 %, calcd. 26.36 %). The remaining mass of 18.54% is metallic Ag, which is compatible with the calculated value of 19.65%.

### 4. Conclusion

Two bis(isopropylimidazole) derivative ligands and their complexes with the Ag(I) ion were synthesized. The results showed that the different aromatic and aliphatic groups inserted on the backbone of the bis(isopropylimidazole) ligands did affect the structures of the synthesized complexes. Crystal analysis showed that complex **1** had a polynuclear structure, whereas complex **2** had a dinuclear structure. The thermal stabilities increased on changing to aromatic groups from aliphatic substitute groups on the imidazole rings. Photoluminescence

spectra of the complexes showed that complex **1** exhibited a more intense emission compared to complex **2**, which could stem from close aromatic interactions between the imidazole rings in complex **1**.

### 5. Supplementary material

Fig. S1. shows the IR spectra of complexes **1** and **2**. Figs. S2 and S3. exhibit the TG, DTA and DTG curves for **1** and **2**, respectively.

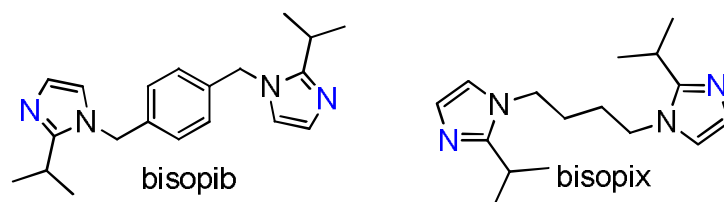
### Acknowledgements

The authors acknowledge the Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

### Appendix A. Supplementary data

CCDC 1487363 and 1487364 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

**Scheme 1.** Bis(isopropyl)imidazole ligands containing aromatic and aliphatic backbones



**Table 1.** Crystal data and structure refinement parameters for complexes **1** and **2**.

Crystal data	<b>1</b>	<b>2</b>
Empirical formula	C <sub>23</sub> H <sub>30</sub> N <sub>5</sub> O <sub>3</sub> SAg	C <sub>54</sub> H <sub>64</sub> N <sub>10</sub> O <sub>8</sub> S <sub>2</sub> Ag <sub>2</sub>
Formula weight	564.45	1261.01
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
<i>a</i> (Å)	15.237(5)	10.4523(9)
<i>b</i> (Å)	13.438(4)	10.5654(9)
<i>c</i> (Å)	13.463(5)	14.9466(2)
$\alpha$ (°)	90.00	105.731(4)
$\beta$ (°)	114.43(2)	98.631(5)
$\gamma$ (°)	90.00	96.425(4)
<i>V</i> (Å <sup>3</sup> )	2509.90(2)	1550.50(2)
<i>Z</i>	4	1
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.494	1.351
$\mu$ (mm <sup>-1</sup> )	0.92	0.76
$\theta$ range (°)	3.0-28.3	3.0-24.0
Measured refls.	39933	66267
Independent refls.	3131	6070
<i>R</i> <sub>int</sub>	0.034	0.053
<i>S</i>	1.05	1.07
R1/wR2	0.056/0.132	0.060/0.199
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (eÅ <sup>-3</sup> )	1.07/-1.44	1.87/-0.50

**Table 2.** Selected FT-IR spectral data for [Ag(sac)], [Ag<sub>2</sub>(sac)<sub>2</sub>(o-bix)<sub>2</sub>], together with complexes **1** and **2** (cm<sup>-1</sup>)

Assignment	[Ag(sac)] [46]	[Ag <sub>2</sub> (sac) <sub>2</sub> (o-bix) <sub>2</sub> ] [47]	{[Ag(sac)(μ-bisopib)] <sub>n</sub> ( <b>1</b> )	[Ag(sac)(μ-pbisopix)] <sub>2</sub> ·2H <sub>2</sub> O ( <b>2</b> )
v(CH) <sub>aliphatic</sub>	-	-	2955m, 2922m, 2862m	2968m, 2930m, 2866m
v(CO)	1640sh, 1612vs	1639vs	1663vs	1651vs
v(CC)	1577vs, 1458s	1583vs, 1454m	1592m	1587m
v <sub>s</sub> (CNS)	1338sh	1328sh	1354sh	1340sh
v <sub>as</sub> (SO <sub>2</sub> )	1284vs, 1258vs	1251vs	1285vs	1269vs
v <sub>s</sub> (SO <sub>2</sub> )	1150vs	1147vs	1153vs	1150vs

Sh = shoulder; w = weak; m = medium; s = strong; vs = very strong.

**Table 3.** Selected bond distances and angles for complexes **1** and **2** (Å, °)

<b>Complex 1</b>			
N3-Ag1	2.164(4)	N1-Ag1	2.282(3)
N3-Ag1-N1	136.29(7)	N1-Ag1-N1 <sup>i</sup>	87.42(15)
<b>Complex 2</b>			
Ag1-N1	2.291(4)	Ag1-N2A	2.254(14)
Ag1-N5 <sup>i</sup>	2.184(4)		
N2A-Ag1-N1	102.0(3)	N5 <sup>i</sup> -Ag1-N2A	137.3(3)
N5 <sup>i</sup> -Ag1-N1	120.68(15)		

Symmetry codes: (i) -x+1, y, -z+3/2 for **1**; (i) -x+1, -y+1, -z for **2**.

**Table 4.** Interaction distances (Å) and angles (°) for selected Ag(I) complexes, including close C-H...Ag(I) interactions

Complexes	d[Ag(I)...H]	d[Ag(I)...C]	a[C-H...Ag(I)]	Ref
<b>1</b>	<b>2.630</b>	<b>3.427</b>	<b>143.12</b>	<b>This work</b>
<b>2</b>	<b>2,715</b>	<b>3,496</b>	<b>138.94</b>	<b>This work</b>
[Ag <sub>2</sub> L1](ClO <sub>4</sub> ) <sub>2</sub>	2.944	3.475	109.0	[27]
[Ag <sub>6</sub> (L2) <sub>6</sub> (dmp) <sub>2</sub> ]	2.823	3.541	134.24	[28]
[Ag <sub>2</sub> (μ-2,3-pydc) <sub>2</sub> (Hpda) <sub>2</sub> ·2H <sub>2</sub> O]	2.811	3.232	106.25	[29]
{[AgL3](ClO <sub>4</sub> ) <sub>2</sub> }	2.657	3.198	116.60-	[30]
[Ag <sub>2</sub> (μ <sub>3</sub> -sac) <sub>2</sub> (μ-nmpen)] <sub>n</sub>	2.684	3.275	119.71	[31]

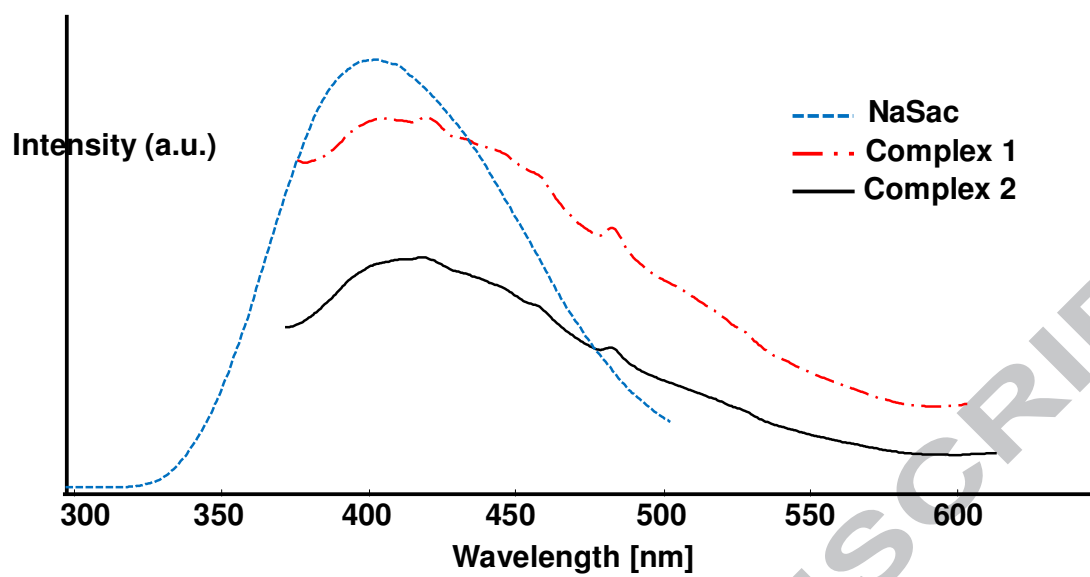
[L1 = hexakis(3-(2-pyridyl)pyrazol-1-ylmethyl)benzene; HL2; anthracene-9-carboxylic acid, dmp = 2,6-dimethylpyridin; 2,3-pydcH<sub>2</sub> = pyridine-2,3-dicarboxylic acid; pda = 1,3-diaminopropane; L3 = 9-[3-(2-pyridyl)pyrazol-1-yl]-acridine; sac = saccharinate; nmpen = N-methyl-1,3-propanediamine]



**Table 5.** Hydrogen-bond parameters for complexes **1-2** (Å, °)

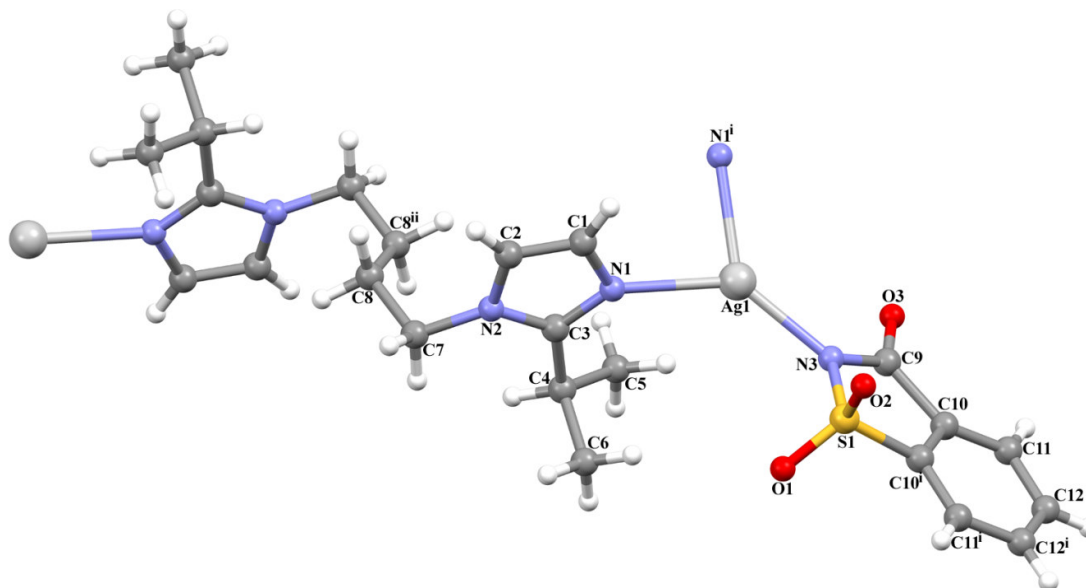
D-H...A	D-H	H...A	D...A	D-H...A
<b>Complex 1</b>				
C2—H2...O1 <sup>iii</sup>	0.93	2.46	3.385(6)	174
C2—H2...O3 <sup>iii</sup>	0.93	2.37	3.221(6)	153
C7—H7A...O2 <sup>iii</sup>	0.97	2.53	3.217(7)	128
C8—H8B...O2 <sup>iii</sup>	0.97	2.55	3.159(10)	121
<b>Complex 2</b>				
C22—H22...O1 <sup>ii</sup>	0.93	2.60	3.472(7)	156
C14—H14B...O1 <sup>iii</sup>	0.97	2.57	3.537(9)	177
C9A—H9A...O2 <sup>iv</sup>	0.93	2.25	3.169(13)	168
O4—H4A...O3 <sup>i</sup>	0.84(1)	2.00(3)	2.725(12)	145
C2—H2...Cg(1) <sup>iv</sup>	0.93	3.21	3.945(3)	136
C27—H27B...Cg(1) <sup>v</sup>	0.96	3.06	3.901(4)	146

Symmetry codes: (iii)  $x, -y+1, z-1/2$  for **1**; (i)  $-x+1, -y+1, -z$ ; (ii)  $x+1, y+1, z$ ; (iii)  $x, y+1, z$ ; (iv)  $-x+1, -y+1, -z+1$ ; (v)  $1-x, 2-y, -z$ ; Cg(1)=C15-C20; for **2**.



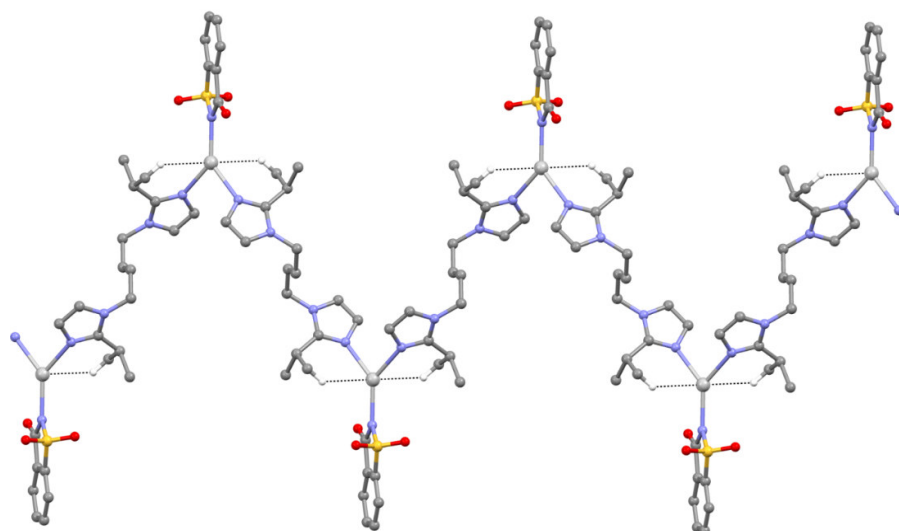
**Fig 1.** Solid state room temperature emission spectra of Na(sac), together with complexes 1 and 2

ACCEPTED MANUSCRIPT

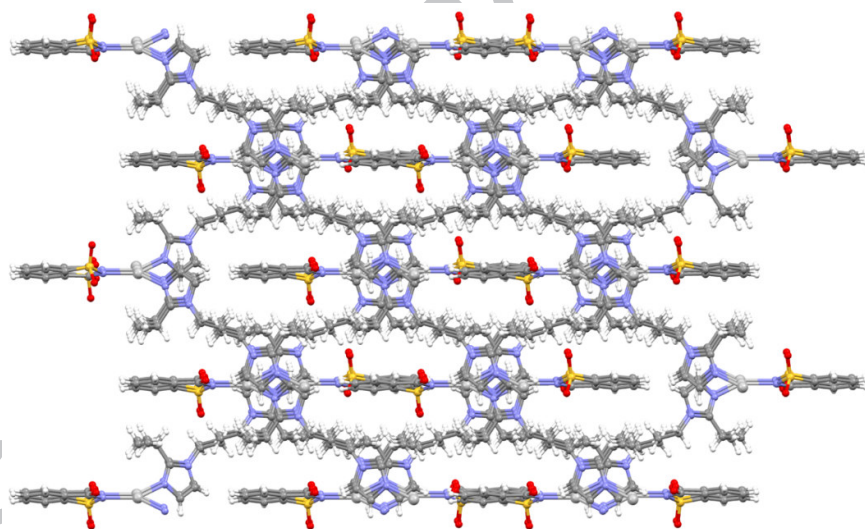


**Fig. 2.** The molecular structure of **1** showing the atom numbering scheme. [(i)  $-x+1, y, -z+3/2$ ;  
(ii)  $-x+1/2, -y+1/2, -z+1$ ]

ACCEPTED MANUSCRIPT

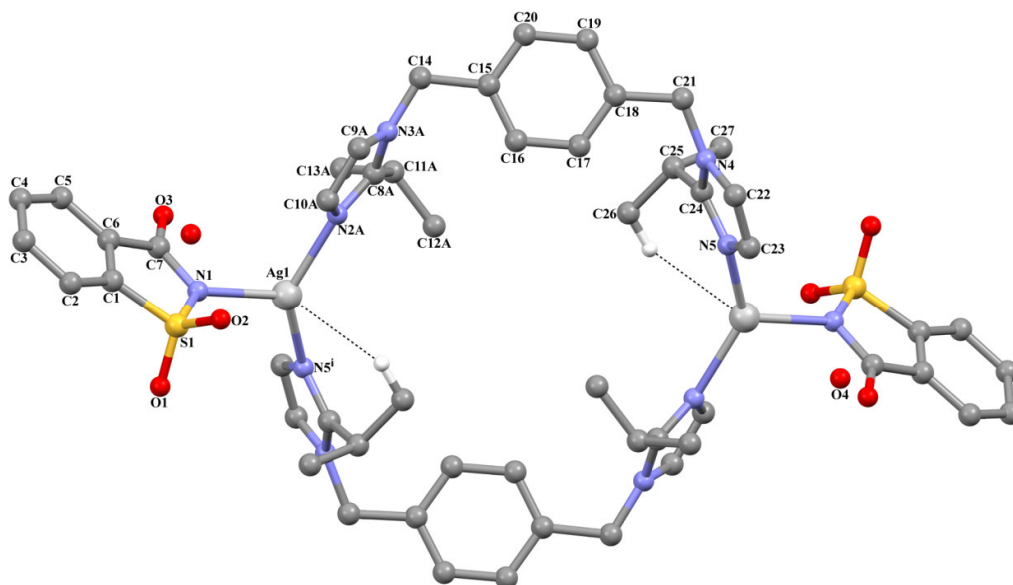


(a)

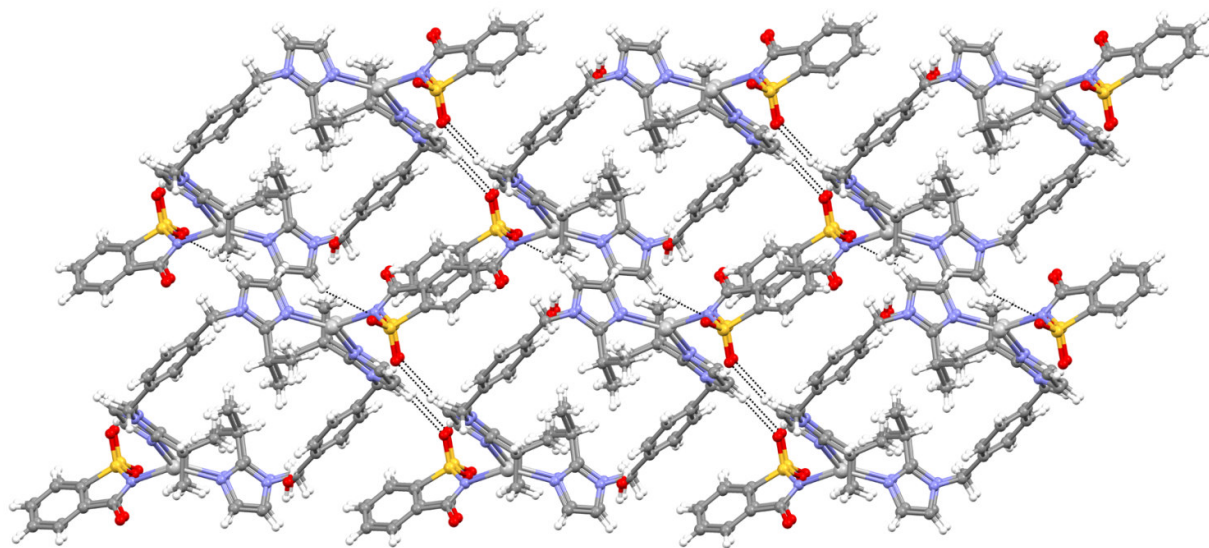


(b)

**Fig. 3.** (a) Zig-zag 1D polymer of **1** with the C-H...Ag(I) interactions. (b) 3D supramolecular network of **1**.



**Fig. 4.** The molecular structure of **2** showing the atom numbering scheme.  $[(i) -x+1, -y+1, -z]$



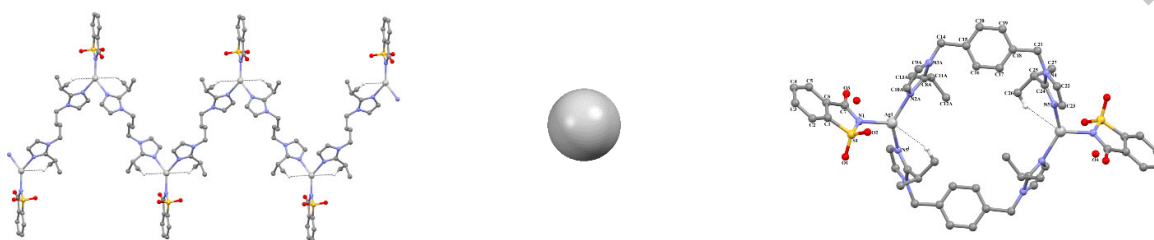
**Fig. 5.** An infinite 2D layer in **2**.

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## Graphical abstract



-  $[\text{Ag}(\text{sac})(\mu\text{-bisopib})]_n$  (**1**) and  $[\text{Ag}(\text{sac})(\mu\text{-bisopix})]\cdot\text{H}_2\text{O}$  (**2**) have been synthesized based on bis(isopropylimidazole) ligands

- Complex **1** shows the closest  $\text{C-H}\cdots\text{Ag}$  interaction distance among similar literature examples

- The  $\text{C-H}\cdots\text{O}$  hydrogen bonds and  $\text{C-H}\cdots\pi$  interactions play a crucial role in the architecture of the 3D network of complex **2**