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Shouwen Jin^a, Daqi Wang^b, Bin Shen^a, Yibin Li^a, Fengbo Yu^a,
Songsong Ji^a & Miaoda Su^c

^a Faculty of Science, Zhejiang A & F University, Donghu Campus,
Lin'An 311300, P.R. China

^b Department of Chemistry, Liaocheng University, Liaocheng,
Shandong 252059 P.R. China

^c School of Engineering, Zhejiang A & F University, Donghu
Campus, Lin'An 311300, P.R. China

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Synthesis and structural characterization of three saccharinate–metal complexes with exo-bidentate bis(imidazole) derivatives

SHOUWEN JIN*†, DAQI WANG‡, BIN SHEN†, YIBIN LI†,
FENGBO YU†, SONGSONG JI† and MIAODA SU§

†Faculty of Science, Zhejiang A & F University, Donghu Campus,
Lin'An 311300, P.R. China

‡Department of Chemistry, Liaocheng University, Liaocheng,
Shandong 252059 P.R. China

§School of Engineering, Zhejiang A & F University, Donghu Campus,
Lin'An 311300, P.R. China

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Three coordination compounds, $[\text{Ag}_2(\text{L}^1)(\text{sac})_2] \cdot 5(\text{H}_2\text{O})$ (**1**, $\text{L}^1 = \text{bis}(N\text{-imidazolyl})\text{methane}$, sac = saccharinate), $[\text{Ag}(\text{L}^2)(\text{sac})]$, (**2**, $\text{L}^2 = 1,4\text{-bis}(N\text{-imidazolyl})\text{butane}$), and $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 2(\text{H}_2\text{O})$ (**3**), were obtained from self-assembly of the metal salts with bis-imidazole ligands in the presence of saccharinato ion. All products were formed in solution and obtained by slow evaporation. Their structures were fully characterized by X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy, elemental analysis, and thermogravimetric analyses. Compound **1** is a linear dinuclear complex, consisting of two Ag(sac) units bridged by a bis(*N*-imidazolyl)methane, while **2** is a tri-coordinated Ag(I) complex, with Ag(I) surrounded by three nitrogens in trigonal plane geometry. Compound **2** displays a 1-D wavy chain structure. XRD analysis revealed that **3** exhibits 1-D cationic double-stranded chain structure from doubly bridged $[\text{Cu}(\text{H}_2\text{O})_2]$ units. All these complexes display 3-D framework structures from a number of non-conventional weak interactions. IR spectra, elemental analyses, and thermal analyses are in good agreement with the crystal structure.

Keywords: Silver(I); Copper(II); Bis-imidazole; Saccharinate; Crystal and molecular structure

1. Introduction

Saccharin ($\text{Hsac} = \text{C}_7\text{H}_5\text{SO}_3\text{N}$, *o*-sulfobenzoimide, or 1,2-benzisothiazole-3(2H)-one-1,1-dioxide) was discovered more than 100 years ago and is one of the best known and most widely used artificial sweeteners. The imino hydrogen of saccharin is acidic and can be readily deprotonated to form the corresponding saccharinato anion. The deprotonated form of saccharin, saccharinate (sac), is a polyfunctional ligand through four sites, the negatively charged imine nitrogen, one carbonyl, and two

*Corresponding author. Email: jinsw@zafu.edu.cn

sulfonyl oxygens. Metal complexes of sac have received much attention due to their physical and chemical properties [1]. Sac can exhibit mono- (N or O), bi- (N, O) or multi-dentate coordination and can form metal complexes ranging from mononuclear to coordination polymers. Sometimes it functions as a counter-ion especially in the presence of relatively bulky ligands. The sac anion participates in the formation of mixed-ligand complexes, sharing coordination spheres with a number of different ligands and showing a variety of binding characteristics. Metal complexes containing sac and nitrogen donors have been studied by various research groups also [2–14]. Metal complexes of sac with bis(*N*-imidazolyl)methane (L^1) and 1,4-bis(*N*-imidazolyl)butane (L^2) have not been reported yet, but may be helpful to understand the coordination behavior of sac in the presence of flexible or semi-flexible secondary ligands. As a part of our continuing research on synthesis and characterization of mixed-ligand complexes bearing bis(*N*-imidazolyl)methane (L^1) and 1,4-bis(*N*-imidazolyl)butane (L^2) [15–18], herein we describe the synthesis, spectral, thermal, and structural characterizations of three new complexes containing saccharinate (sac) and exo-bidentate imidazolyl derivatives, namely $[Ag_2(L^1)(sac)_2] \cdot 5(H_2O)$ (**1**, $L^1 = \text{bis}(N\text{-imidazolyl)methane}$), $[Ag(L^2)(sac)]$ (**2**, $L^2 = 1,4\text{-bis}(N\text{-imidazolyl)butane}$), and $[Cu(L^2)_2(H_2O)_2](sac)_2 \cdot 2(H_2O)$ (**3**).

2. Experimental

2.1. Materials

Bis(*N*-imidazolyl)methane (L^1) and 1,4-bis(*N*-imidazolyl)butane (L^2) [19] were prepared according to literature procedures. All other reagents were commercially available and used as received.

2.2. Physical measurements and analyses

C, H, N, and S elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. FT-IR spectra were recorded from KBr pellets (4000–400 cm^{-1}) on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analyses (TGA) were studied by a Delta Series TA-SDT Q600 in a N_2 atmosphere from room temperature to 800°C (heating rate = 10°C min^{-1}) using Al crucibles.

2.3. Preparation of the compounds

2.3.1. Preparation of $[Ag_2(L^1)(sac)_2] \cdot 5(H_2O)$ (1**).** Solid $Na(sac) \cdot 2H_2O$ (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 : 1) with stirring. The solution immediately became milky. After the addition of L^1 (0.148 g, 1 mmol) in 10 mL distilled water, a suspension with a white precipitate was formed; the suspension was stirred for 1 h in the dark. Then to this suspension a few drops of concentrated ammonia was added until a clear solution resulted. The solution was kept in darkness at room temperature and colorless single crystals of $[Ag_2(L^1)(sac)_2] \cdot 5(H_2O)$ were obtained after several days. Yield 0.66 g, 80.7% (based on L^1). Anal. Calcd for $C_{21}H_{26}Ag_2N_6O_{11}S_2$

(MW = 818.34) (%): C, 30.79; H, 3.18; N, 10.26; S, 7.82. Found (%): C, 30.78; H, 3.12; N, 10.20; S, 7.78. IR (KBr disc, cm^{-1}): 3535 s, 3236 s, 3105 m, 3010 w, 2244 m, 1649 vs, 1497 m, 1383 s, 1351 w, 1279 m, 1230 s, 1150 s, 1085 s, 1030 w, 932 m, 831 m, 768 s, 714 m, 652 m, 613 w.

2.3.2. Preparation of $[\text{Ag}(\text{L}^2)(\text{sac})]$ (2). Solid $\text{Na}(\text{sac}) \cdot 2\text{H}_2\text{O}$ (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 : 1) with stirring. The solution immediately became milky. After the addition of L^2 (0.190 g, 1 mmol) dissolved in 10 mL of ethanol, a suspension with a white precipitate was formed; the suspension was stirred for 1 h in the dark. Then to this suspension a few drops of concentrated ammonia was added until a clear solution resulted. The solution was kept in darkness at room temperature and colorless single crystals of $[\text{Ag}(\text{L}^2)(\text{sac})]$ were obtained after several days. Yield 0.36 g, 75%. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{AgN}_5\text{O}_3\text{S}$ (MW = 480.29) (%): C, 42.47; H, 3.75; N, 14.57; S, 6.66. Found (%): C, 42.42; H, 3.69; N, 14.53; S, 6.61. IR (KBr disc, cm^{-1}): 3100 vw, 3072 w, 2942 w, 1646 vs, 1518 m, 1460 w, 1449 w, 1363 m, 1292 m, 1275 s, 1236 w, 1152 vs, 1123 m, 1087 m, 934 w, 823 w, 768 m, 742 m, 658 w, 625 w.

2.3.3. Preparation of $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 2(\text{H}_2\text{O})$ (3). To a solution of sodium saccharinate (2 mmol, 0.482 g) dissolved in 10 mL distilled water a solution of $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.25 g, 1 mmol) dissolved in water (20 mL) was added dropwise with stirring. The stirring was continued for 1 h. Then, after the addition of 5 mL of L^2 (0.380 g, 2 mmol) in ethanol, a suspension with a blue precipitate was formed; the suspension was stirred at room temperature for 2 h. Then to the suspension a few drops of concentrated ammonia was added until a clear dark blue solution resulted; the solution was kept at room temperature and dark blue block crystals of $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 2(\text{H}_2\text{O})$ were obtained after several days. Yield 0.73 g, 82.9% (based on Cu). Anal. Calcd for $\text{C}_{34}\text{H}_{44}\text{CuN}_{10}\text{O}_{10}\text{S}_2$ (MW = 880.45) (%): C, 46.34; H, 4.99; N, 15.90; S, 7.27. Found (%): C, 46.31; H, 4.94; N, 15.88; S, 7.24. IR (KBr disc, cm^{-1}): 3425 vs, 3213 s, 3115 w, 3072 w, 2942 w, 2242 w, 1642 vs, 1504 s, 1392 m, 1277s, 1234 s, 1151 vs, 1101 w, 1087 s, 1032 w, 932 m, 842 m, 766 m, 734 w, 658 m, 634 w.

2.4. Structure determination

Suitable crystals were mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo- $\text{K}\alpha$ radiation (0.71073 Å). Data collection and reduction were performed using *SMART* and *SAINT* software [20]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using *SHELXTL* [21]. Hydrogen positions for all the structures were located in a difference map and refined independently. Further details of the structural analyses are summarized in table 1. Selected bond lengths and angles for **1–3** are listed in table 2. Relevant hydrogen bonds are listed in table 3.

Table 1. Crystal data and structure refinement summary for 1–3.

	1	2	3
Formula	C ₂₁ H ₂₆ Ag ₂ N ₆ O ₁₁ S ₂	C ₁₇ H ₁₈ AgN ₅ O ₃ S	C ₃₄ H ₄₄ CuN ₁₀ O ₁₀ S ₂
Formula weight	818.34	480.29	880.45
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P2(1)/n</i>	<i>Pī</i>
Unit cell dimensions (Å, °)			
<i>a</i>	11.0302(11)	7.4349(8)	8.4601(10)
<i>b</i>	12.4236(15)	18.7203(14)	10.1500(13)
<i>c</i>	20.653(2)	13.2271(11)	11.6109(15)
α	90.00	90	85.995(2)
β	95.9430(10)	95.5920(10)	77.3710(10)
γ	90.00	90	78.7030(10)
Volume (Å ³), <i>Z</i>	2815.0(5), 4	1832.2(3), 4	953.7(2), 1
Calculated density (Mg m ⁻³)	1.931	1.741	1.533
Absorption coefficient (mm ⁻¹)	1.608	1.243	0.753
<i>F</i> (000)	1632	968	459
Crystal size (mm ³)	0.42 × 0.35 × 0.34	0.18 × 0.11 × 0.09	0.49 × 0.44 × 0.34
θ range for data collection (°)	1.98–25.02	1.89–25.02	1.80–25.01
Reflections collected	6689	9582	4937
Independent reflection	2466 [<i>R</i> (int) = 0.1021]	3230 [<i>R</i> (int) = 0.0895]	3299 [<i>R</i> (int) = 0.0199]
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Goodness-of-fit on <i>F</i> ²	1.190	1.052	1.043
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0781; <i>wR</i> ₂ = 0.2391	<i>R</i> ₁ = 0.0662; <i>wR</i> ₂ = 0.1823	<i>R</i> ₁ = 0.0389; <i>wR</i> ₂ = 0.0991
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0956; <i>wR</i> ₂ = 0.2541	<i>R</i> ₁ = 0.0910; <i>wR</i> ₂ = 0.1957	<i>R</i> ₁ = 0.0532; <i>wR</i> ₂ = 0.1111

Table 2. Selected bond lengths (Å) and angles (°) for 1–3.

1			
Ag(1)–N(3)	2.103(8)	Ag(1)–N(1)	2.123(8)
N(3)–Ag(1)–N(1)	167.6(3)		
2			
Ag(1)–N(3)	2.206(6)	Ag(1)–N(5)	2.211(6)
Ag(1)–N(1)	2.249(7)	N(3)–Ag(1)–N(5)	125.7(3)
N(3)–Ag(1)–N(1)	116.2(2)	N(5)–Ag(1)–N(1)	117.9(2)
3			
Cu(1)–N(3)	2.011(2)	Cu(1)–N(5)#2	2.047(2)
Cu(1)–O(4)	2.496(2)	N(3)#1–Cu(1)–N(5)#2	87.52(9)
N(3)#1–Cu(1)–N(5)#3	92.48(9)	N(3)–Cu(1)–O(4)	89.39(9)
N(3)#1–Cu(1)–O(4)	90.61(9)	N(5)#2–Cu(1)–O(4)	90.94(8)
N(5)#3–Cu(1)–O(4)	89.06(8)		

Symmetry codes for 3: #1 $-x, -y+1, -z+1$; #2 $-x, -y+2, -z+1$; #3 $x, y-1, z$.

3. Results and discussion

3.1. Preparation and general characterization

Complexes **1** and **2** were readily prepared by direct reaction of AgNO₃ and Na(sac)·2H₂O in the presence of the corresponding L¹ or L² in the dark at room temperature and obtained in yields of over 75%. Single crystals of **1** and **2** suitable for

Table 3. Hydrogen bond distances (Å) and angles (°) in **1** and **3**.

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
1				
O(5)–H(5D)...O(1)#2	0.85	2.10	2.952(12)	179.6
O(5)–H(5C)...O(6)	0.85	1.96	2.809(13)	179.4
O(4)–H(4D)...O(5)#3	0.85	2.02	2.862(13)	169.3
O(4)–H(4C)...O(5)#4	0.85	2.02	2.862(13)	169.3
3				
O(5)–H(5D)...O(1)#5	0.85	2.02	2.871(5)	179.6
O(5)–H(5C)...O(1)#6	0.85	2.46	3.306(6)	178.4
O(4)–H(4D)...O(3)	0.85	1.99	2.839(3)	175.9
O(4)–H(4C)...N(1)#7	0.85	2.10	2.949(3)	175.9

Symmetry transformations used to generate equivalent atoms for **1**: #2 $-x+1, y, -z+1/2$; #3 $-x+3/2, y-1/2, -z+1/2$; #4 $x-1/2, y-1/2, z$. Symmetry transformations used to generate equivalent atoms for **3**: #5 $-x+2, -y+1, -z+1$; #6 $x, y, z+1$; #7 $-x+1, -y+1, -z+1$.

X-ray diffraction analysis were obtained by slow evaporation of their ammonia solution. Compound **3** was prepared similar to **1** and **2** but using CuSO₄ instead of AgNO₃; its crystals were also obtained by slow evaporation of its ammonia solution. The compositions of these complexes were determined by elemental and TG analyses. Elemental analyses were consistent with their proposed formulae. The three complexes are non-hygroscopic and stable in air at ambient temperatures, but both **1** and **2** are somewhat light sensitive. The complexes are insoluble in water and common organic solvents, such as methanol or ethanol. Strong and broad features at 3400–3100 cm⁻¹ in IR spectra of **1** and **3** arise from O–H stretching frequencies of water. The stretching vibrations of μ -asym·(SO₂) and μ -sym·(SO₂) occur at *ca* 1280 and 1150 cm⁻¹, respectively. For **1**, **2**, and **3** the absorption bands of the carbonyl of sac appear at *ca* 1642 cm⁻¹ as a very strong single band.

3.2. Structural descriptions

3.2.1. X-ray structure of [Ag₂(L¹)(sac)₂]·5(H₂O) (1**).** The preparation of **1** was carried out with bis(*N*-imidazolyl)methane, AgNO₃, and sodium saccharinate in 1 : 1 : 1 ratio. The colorless block crystals suitable for X-ray diffraction analysis were grown by slow evaporation of its ammonia solution. The crystal structure of **1** consists of one [Ag₂(L¹)(sac)₂] unit and five free water molecules. The asymmetric unit contains only half of its formula content. Each Ag is coordinated by one imidazolyl nitrogen from one L¹ and one imine nitrogen of sac anion to form a AgN₂ binding set, as shown in figure 1. The Ag displays an almost linear geometry with N–Ag–N angle of 167.6(3)°. X-ray diffraction analysis shows **1** to be a dinuclear complex, in which sac is a monodentate terminal ligand, while L¹ is bidentate and bridging *via* nitrogens; L¹ adopts *trans* configuration.

The Ag–N_{imidazole} bond distance (table 2) is very similar to those found for other silver(I) complexes containing imidazole-type ligands [10, 22]. The Ag–N_{sac} bond distance is also comparable to those reported for several silver(I)-sac complexes [23–28], but significantly shorter than the corresponding distances of 2.285(8) and

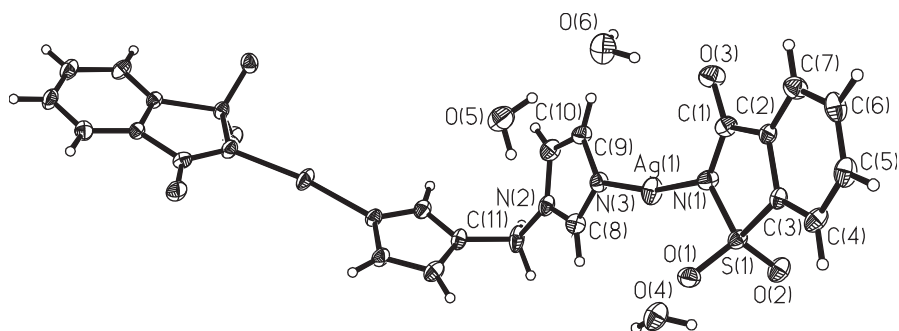


Figure 1. Local coordination environment around Ag in **1** with the atom numbering scheme. The thermal ellipsoids are drawn at 30% probability.

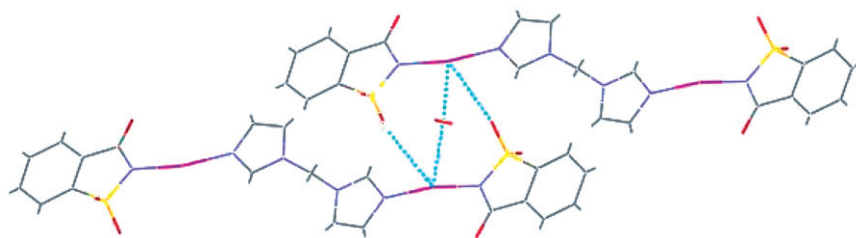


Figure 2. The coordination environment of Ag provided by two Ag–N coordination bonds, two weak Ag–O interactions, and one Ag–C interaction.

2.449(2) Å found in [Ag(sac)(PPh₃)₂] [29] and [Ag₂(sac)₂(μ-aepy)₂] [30], respectively. The Ag–N_{sac} bond distance is slightly longer than the Ag–N_{imidazole} bond distance.

The two imidazole rings in L¹ are almost perpendicular to each other with dihedral angle of 99.08(13)°. The sac ligand is roughly planar with an r.m.s. deviation of the non-hydrogen atoms (excluding the sulfonyl O) from the best least square plane of approximately 0.0154 Å, the dihedral angle between the five-membered ring, and the benzene ring in the same sac is 1.7°. The dihedral angle between the imidazole ring and the sac anion coordinated to the same Ag ion is 173.8°, indicating the co-planarity of both rings.

Discrete dinuclear moieties are linked by weak Ag–O_{sulfonyl} bonds in which the distance is 3.06 Å, similar to other weak Ag–O_{carbonyl} interactions (3.07–3.09 Å) existing in parallel chains of {[Ag(3-impmd)]·(SbF₆)·CH₂Cl₂}_∞ (3-impmd is *N,N'*-bis(3-imidazol-1-yl-propyl)-pyromellitic diimide) [31]. The Ag–O_{sulfonyl} distance is significantly longer than the bridging Ag–O_{sulfonyl} bond distance in the dinuclear silver complex containing the sac ligand [26].

There are also Ag–O_{water} interactions with Ag–O_{water} distance of 2.891 Å, thus the Ag⁺ may be viewed as a tetrahedron with a AgN₂O₂ binding (figure 2). 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. There is one C–H···O interaction between CH of sac and water molecules in which the C–O distance is 3.382 Å. There are two C–H···O interactions arising from the sulfonyl group, one between the sulfonyl group and the methylene linker of L¹ with C–O distance of 3.097 Å, the other between

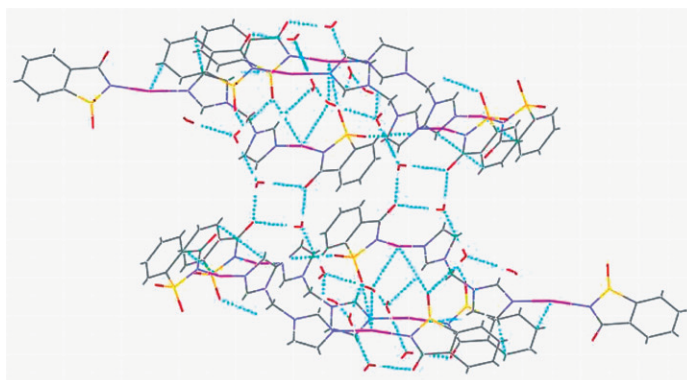


Figure 3. 3-D framework structure of **1** viewed from the *b*-axis.

the sulfonyl group and 4-CH of imidazole with C–O distance of 3.334 Å. In the lattice, water molecules form pentamers through intermolecular O–H...O hydrogen bonds (table 3). In such water pentamers, the two water molecules located at the terminal position form two O–H...O hydrogen bonds with the carbonyl of sac, and the second water molecule formed only one 2-CH_{imidazole}–O hydrogen bond, while the middle water molecule functioned as a bridged bidentate ligand coordinated to two silvers simultaneously. The middle water molecule also formed two hydrogen bonds through both of its hydrogens with two adjacent water molecules. Terminal water molecules in two adjacent water pentamers and two carbonyl oxygens from two dinuclear units form a four-membered ring through four O–H...O hydrogen bonds.

The Ag–Ag distance in the dinuclear moiety is 9.706 Å, while the distance between two neighboring units bridged by the semi-coordinated water is 4.845 Å precluding Ag–Ag interaction. There also exist π – π interactions between benzene of sac and imidazole of adjacent dinuclear moieties in which the centroid–centroid separation is *ca* 3.388 Å. X-ray structural analysis shows that there are weak Ag... π interactions between silver(I) and benzene of neighboring dinuclear molecules with the Ag–Cg distance of 3.251 Å, which is comparable with the corresponding value of Ag₂(L5v)₂(SbF₆)₂ [L5v = (3-methoxy-4-hydroxyphenyl)bis(3,5-dimethylpyrazolyl) methane, in which the Ag–centroid distance is 3.2 Å] [32]. All these weak interactions give a 3-D network structure, shown in figure 3.

3.2.2. Crystal structure of [Ag(L²)(sac)] (2). In anhydrous [Ag(L²)(sac)] **2**, the silver adopts a slightly distorted trigonal planar geometry with the N–Ag–N bond angles slightly deviating from 120° (table 2). Each Ag is coordinated by two imidazolyl nitrogens from two L² ligands and one nitrogen from sac to form a AgN₃ binding set, shown in figure 4. The Ag–N_{sac} bond distance is similar to those found in three-coordinate silver, [Ag(sac)(pyz)]_n (2.216(2) Å, pyz = pyrazine) [1], and [Ag₂(C₇H₄NO₃S)₂(C₄H₄N₂)₂] (C₄H₄N₂ = pyridazine, 2.2099 Å) [33], but significantly shorter than the reported value for [Ag₂(sac)₂(μ -aepy)₂] (2.449 Å, aepy = 2-(2-aminoethyl)pyridine) [29]. The Ag–N_{imidazole} bond distances are in the range of the Ag–N_{imidazole} bond length of trigonal coordinated silver [34]. The imidazole rings in **2** are *trans* with respect

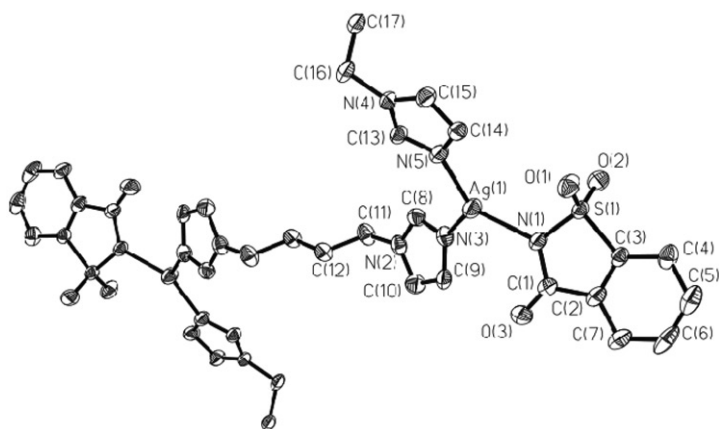


Figure 4. Local coordination environment around Ag in **2** with the atom numbering scheme. The thermal ellipsoids are drawn at 30% probability.

to C17–C17a and C12–C12a bonds (angles C16–C17–C17a–C16a and C11–C12–C12a–C11a both are 180°), the same as L², which shows that the coordination of the imidazole nitrogen causes no significant change in the conformation of L² in this compound [35].

The dihedral angle between the two imidazole planes in the same L² is 79.73(13)°, while the dihedral angle between two imidazole planes in different L² is 35.4°. The sac is also planar with an r.m.s deviation of 0.0131 Å and dihedral angle between the five-membered ring and benzene ring in the same sac is 1.5°. The sac ion makes angles of 23° and 40.1° with both imidazole rings of L².

The structure of **2** consists of a 1-D wavy chain, and the Ag ions at the wave crest and the wave trough are linearly arranged along the crystallographic *b*-axis. The distances between two Ag atoms at two adjacent wave crests or wave troughs are 18.720 Å, equal to the *b*-axis length of the unit cell, whereas the Ag...Ag distances bridged by L² are 14.350 Å. The Ag...Ag...Ag angles are 82.67°. The closest Ag–Ag distance between neighboring parallel wavy chains is 10.002 Å. Such 1-D chains run parallel to each other in the extended lattice in the *bc* plane. Adjacent chains were connected through C–H...O interaction between the C=O of sac and 4-CH of imidazole on one L² in which the C–O distance is 3.374 Å. Non-conventional weak C–H...O interactions extend the individual 1-D polymeric wavy chains to form a 2-D sheet structure as shown in figure 5. There are Ag– π interactions between adjacent parallel 2-D sheets in which the Ag–centroid distance is 3.139 Å. Compared to **1**, the Ag– π interactions in **2** are much stronger.

Additionally, the polymeric 2-D sheet layers are further connected by non-conventional weak C–H...O interactions with C–O distances ranging from 3.232 to 3.394 Å, that is, there are C–H...O interaction between N–CH–N and the sulfonyl (the C–O distance is 3.394 Å), C–H...O interaction between the benzene CH on sac and sulfonyl (with the C–O distance of 3.232 Å), and C–H...O interaction between CH₂ of the butane spacer and sulfonyl (the C–O distance is 3.327 Å). There are also CH... π interactions existing between CH₂ of the butane spacer and the imidazole ring between two neighboring sheets.

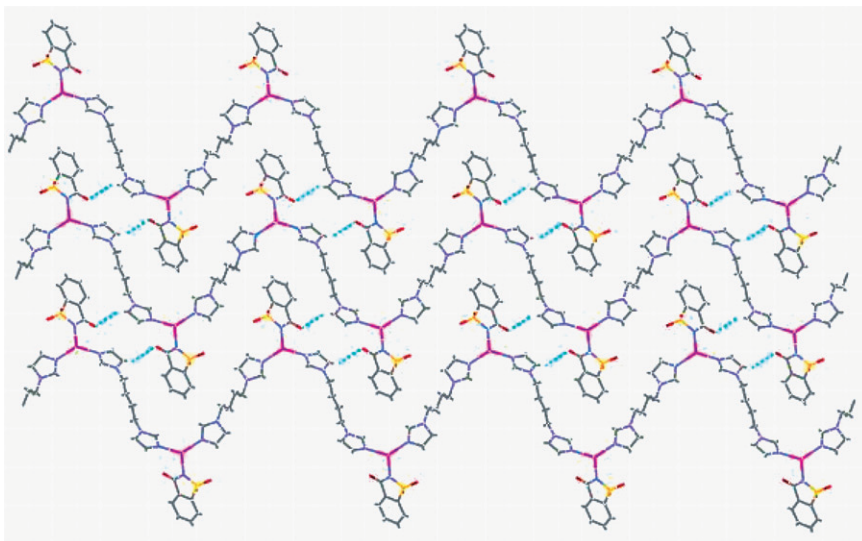


Figure 5. 2-D sheet structure of **2** formed by non-conventional weak C–H...O interactions viewed along the *a*-axis.

The sheets stack approximately along the crystallographic *a*-axis to form a 3-D layer structure in which the closest Ag–Ag distance between the first layer and the second layer is 7.269 Å, while the corresponding distance between the first layer and the third layer is 7.435 Å. In addition, the second sheet layer slips some distance from the first sheet layer, while the third sheet layer has the same projection on the *bc* plane as the first sheet layer.

3.2.3. Crystal structure of $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 2(\text{H}_2\text{O})$ (3**).** When L^2 reacts with sodium saccharinate and $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ in the ratio of 2:2:1, crystals of $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot 2(\text{H}_2\text{O})$ (**3**) suitable for X-ray analysis were isolated by slowly evaporating its ammonia solution. The whole molecule of **3** consists of $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})_2]^{2+}$, two free sac anions, and two free water molecules. Figure 6 exhibits the crystal structure of **3** together with the atom-numbering scheme.

X-ray crystallographic analysis shows that copper(II) in **3** is in an octahedral coordination sphere, in which four crystallographically equivalent L^2 are situated in the plane about Cu, and two crystallographically equivalent water molecules occupy axial positions. The significant difference of **1**, **2**, and **3** is that the saccharinate in **3** is a free counter anion. As in **1** and **2**, L^2 in **3** is bidentate-bridging. Due to the symmetry, the copper and the four nitrogen donors form a perfect plane. Each Cu(II) is linked to four 1,4-bis(*N*-imidazolyl)butane ligands. The Cu–N_{imidazole} bond distances of 2.011(2)–2.047(2) Å are normal and consistent with those of known Cu–imidazole complexes [36]. The N–Cu–N bond angles are close to 90°, similar to a compound with CuN_4O_2 chromophore [7]. The Cu–O_{water} bond distance is within the range of the recently published result [37], but somewhat longer than other Cu complexes, $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2](\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (L = 1,3,5-tris(1-imidazolyl)benzene) [34], and

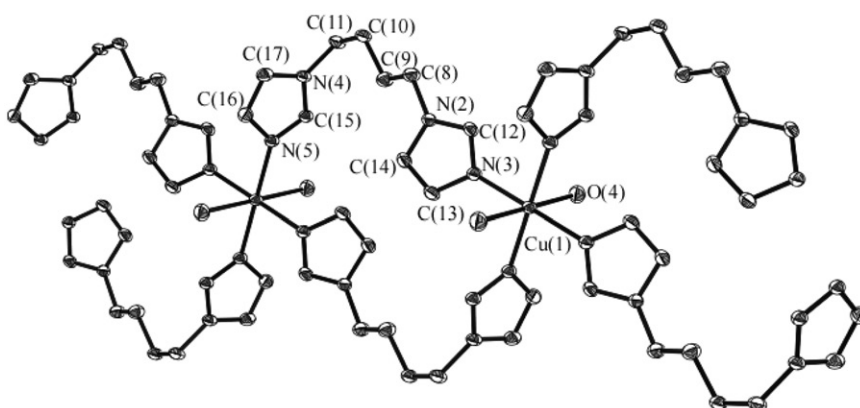


Figure 6. Local coordination environment of Cu in **3** with the atomic numbering scheme. The atoms are drawn with 30% probability ellipsoids; the anions are omitted for clarity.

$[\text{Cu}(\text{L}^1)_2(\text{H}_2\text{O})_2]\text{Cl}_2(\text{H}_2\text{O})_{0.5}(\text{acetone})\}_n$ [38]. The equatorial Cu–N bond lengths are shorter than those of the axial Cu–O due to the Jahn–Teller effect. Thus the coordination geometry of the Cu(II) ion can be regarded as a distorted octahedron. Although the C8–C9–C10–C11 angle (178.16°) is similar to the corresponding angle in free L^2 , the conformation of **3** is significantly different from free L^2 [35], and it is also different from L^2 in **2**.

The imidazole rings form dihedral angles of 93.4° and 43.7° with the plane defined by the carbons of the $-(\text{CH}_2)_4-$ aliphatic linker, which is different from the corresponding value in 1,1'-(butane-1,4-diyl)diimidazolium dinitrate [39]. The interplane angle between the two imidazole planes in the same L^2 is 114.7° . The sac ion makes angles of 94.7° and 44.2° with both imidazole rings of L^2 showing approximately perpendicular arrangement of the sac ring and one imidazole.

The structure of **3** consists of 1-D cationic double-stranded chains; in the chains there are 24-membered rings formed by two copper cations and two bridged L^2 , in which the Cu–Cu separation in the 24-membered ring is 10.150 \AA . To the best of our knowledge this is the first case that the flexible ligand L^2 formed a double-stranded chain structure with a transition metal. The closest distance between Cu's in neighboring parallel cationic chains is 8.460 \AA . The structure of **3** is different from $[\text{Cu}(\text{L}^2)_2(\text{H}_2\text{O})](\text{NO}_3)_2$ containing L^2 which displays (4, 4) network structure [40]. There are intrachain $\text{CH} \cdots \pi$ and edge to face π – π interactions with the corresponding distance of 3.167 – 3.342 \AA .

Like the reported saccharin complex $[\text{Zn}(\text{phen})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$ (phen = 1,10-phenanthroline) [41], this complex is also an example of “cation–anion pair” through hydrogen bonds that is highly directional. In addition to classical hydrogen bonds between the cation and anion, there are also plenty of non-bonded weak interactions, such as π – π and $\text{CH} \cdots \text{O}$ interactions.

Uncoordinated sac anions were bound to the double-stranded cation chains through $\pi(\text{sac})$ – $\pi(\text{imidazole})$ interaction ($\text{C}_g \cdots \text{C}_g = 3.324 \text{ \AA}$), $5\text{-CH}_{\text{imidazole}}$ – $\pi(\text{sac})$ interaction ($\text{C} \cdots \text{C}_g = 3.472 \text{ \AA}$), $2\text{-CH}_{\text{imidazole}} \cdots \text{O}$ interaction (the C–O distance is 3.400 \AA), and $\text{O-H} \cdots \text{N}$ hydrogen bond ($\text{O}(4)\text{-H}(4\text{C}) \cdots \text{N}(1)\#7$). The saccharinates are sandwiched between two cationic chains with the cationic chains and anions connected through $\text{O-H} \cdots \text{O}$ hydrogen bonds between coordinated water and carbonyl of sac to form

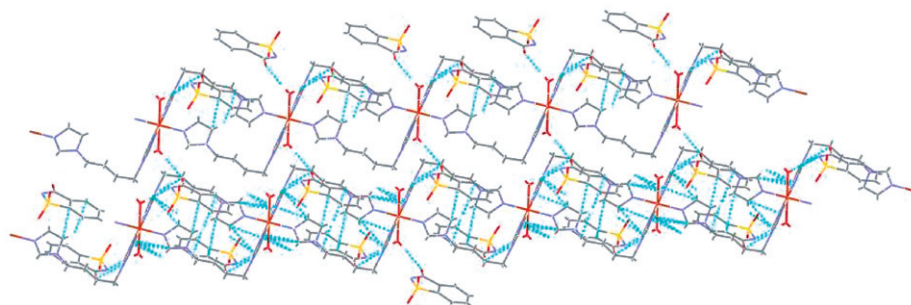


Figure 7. 3-D layer structure of **3**.

a 3-D layer structure (figure 7). The anions and cationic chains were stacked along the *a*-axis alternatively, such that the double-stranded chains were stacked in such a manner that their projection in the *bc* plane is almost completely overlapped as do the anions.

3.3. Thermal properties

TGA of **1** show that dehydration starts at 62°C and all water molecules are lost at 108°C (the calculated weight loss corresponding to five water molecules is 10.99% for **1**, found 10.88%), while the latter step occurs in the range 299°C–342°C with a weight loss of 17.99% due to loss of one L¹ (Calcd 18.08%). The third weight loss of 44.32% from 365°C to 515°C is assigned to loss of two sac ions (Calcd 44.48%). The decomposition ends at 515°C, giving a final decomposition product of metallic silver (total mass loss: found 73.19%, Calcd 73.55%).

TG studies show that silver(I) complex **2** is stable to 260°C and then begins to decompose in three distinct stages. The elimination of L² takes place in the first decomposition stage between 260 and 330°C with a mass loss of 39.51% (Calcd 39.56%). Decomposition of sac begins at 375°C and ends at 545°C with weight loss of 37.83% (Calcd 37.89%), giving a final decomposition product of metallic silver (total mass loss: found 77.34%, Calcd 77.45%).

The TGA traces for **3** showed the first stage between 60 and 132°C corresponds to dehydration with coordinated and uncoordinated water removed in a single stage with a mass loss of 8.02% (Calcd 8.17%). The mass loss between 323 and 478°C may be attributed to loss of two L² and two free sac anions (observed 82.65%, Calcd 84.50%). The final decomposition product is CuO, which is formed by the oxygen uptake from the sac ion (observed 9.02%, Calcd 9.08%).

4. Conclusions

Three coordination polymers containing saccharinate and bis-imidazole with different topologies have been synthesized and structurally characterized. The saccharinates can

be coordinated through only nitrogen (**1**, **2**) or act as counter anions (**3**). The central metal ions are coordinated in $N_2(N_2O_2)$, N_3 , and N_2O_4 fashions. Both bis(*N*-imidazolyl)methane and 1,4-bis(*N*-imidazolyl)butane are bidentate-bridging ligands. The three coordination compounds exhibit dinuclear, 1-D single chain, and 1-D cationic double-stranded chain structures. For the silver compounds, there exist Ag– π interactions with Ag–Cg distances ranging from 3.139 to 3.251 Å. Complex **3** is an example for the formation of “cation–anion pair” through weak interactions, such as classical hydrogen bonds and non-conventional hydrogen bonds.

In all the compounds there are non-conventional C–H...O interactions. This work demonstrates that exo-bis(imidazole) ligands are capable of coordinating to metal atoms with both imidazolyl nitrogen atoms in bidentate-bridging fashion to result in novel motifs, which were further stacked by intermolecular weak interactions to form 3-D frameworks.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 765308 for **1**, 765312 for **2**, and 765442 for **3**. Copies of this information may be obtained free of charge (Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>).

Acknowledgments

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