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Di- and tetranuclear silver (I)-saccharinate complexes with 2-pyridineethanol and 2-pyridinepropanol: Syntheses, crystal structures, spectroscopic and thermal analyses of [Ag₂(sac)₂(pyet)₂] and [Ag₄(sac)₄(pypr)₂]

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Abstract

Two new (saccharinato)silver (I) complexes, $[Ag_2(sac)_2(pyet)_2]$ and $[Ag_4(sac)_4(pypr)_2]$ (sac = saccharinate, pyet = 2-pyridineethanol and pypr = 2-pyridinepropanol), have been prepared and characterized by elemental analyses, IR, thermal analysis and single crystal X-ray diffraction. Both complexes crystallize in triclinic space group of $P\overline{1}$. In $[Ag_2(sac)_2(pyet)_2]$, two monomeric $[Ag(sac)_2(pyet)]$ units are doubly bridged by the sulfonyl oxygen atoms of the sac ligands, forming an $[Ag_2(sac)_2(pyet)_2]$ dimer, in which each silver (I) centre is three coordinate with a T-shaped coordination and the $Ag \cdots Ag$ separation is 5.205 Å. The dimeric units are connected by strong O–H···O_{sulfonyl} intermolecular hydrogen bonds into a one-dimensional chain running parallel to *b*. The one-dimensional hydrogen bonded chains are further linked by $\pi(sac)-\pi(pyet)$ stacking interactions. The tetranuclear complex, $[Ag_4(sac)_4(pypr)_2]$, is achieved by bridging of $[Ag_2(sac)_2]$ with two [Ag(sac)(pypr)] units through the sulfonyl oxygen atoms of the sac ligands. The two silver (I) ions in the centre with a short Ag–Ag bond distance of 2.8480(13) Å exhibit a T-shaped geometry with three sac ligands, while the two terminal silver (I) ions are coordinated by a sac ligand and a pypr ligand in a near linear geometry. The tetranuclear units are held together by O–H···O and C–H···O hydrogen bonds. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Saccharinate; 2-Pyridineethanol; 2-Pyridinepropanol; Dinuclear and tetranuclear silver (I)

1. Introduction

Saccharin, alternatively named 1,2-benzisothiazoline-3-(2H) one 1,1-dioxide or *o*-sulphobenzimide in the form of its water soluble sodium salt, is widely used as a non-caloric sweetener and food additive [1]. The coordination chemistry of saccharin is interesting. Although no metal complexes of neutral saccharin are known, the

corresponding, deprotonated, saccharinate anion (sac) acts as a polyfunctional ligand due to the presence of the negatively charged imino nitrogen, carbonyl oxygen and sulfonyl oxygen atoms. The most common coordination mode of sac is ligation through the nitrogen atom, usually observed in the aquabis(saccharinato) complexes of divalent transition metals [2–6] and coordination via the carbonyl or sulfonyl oxygen is less common.

In recent years, we have investigated the synthesis, spectroscopic, thermal and structural properties of transition metal complexes of sac with substituted pyridine

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ligands, especially those containing additional donor groups such as alkylhydroxyl and alkylamine. We have recently focused our investigations into the complexation of sac with silver (I), since these species are very rare and only two silver (I) complex of sac, [Ag(sac)] [7] and [Ag(sac)(PPh_3)₂] [8] have appeared previously in the literature. Recently, we reported the two new silver (I)-saccharinato complexes Na[Ag(sac)] [9] and [Ag₂(μ -sac)₂ (μ - hep)₂]_n, where hep is N-(2-hydroxyethyl)piperazine [10]. In this study, we report the synthesis, spectroscopic and thermal characterizations and crystal structures of two new (saccharinato)silver (I) complexes with 2-pyridineethanol (pyet) and 2-pyridinepropanol (pypr), namely [Ag₂(sac)₂(pyet)₂] and [Ag₄(sac)₄(pypr)₂].



2. Experimental

2.1. Materials

AgNO₃, Na(sac) \cdot 2H₂O, pyet and pypr were purchased commercially and used as received.

2.2. Preparation of the silver (I) complexes

Pyet (0.12 g, 1 mmol) was added to an aqueous solution (20 ml) of AgNO₃ (0.17 g, 1 mmol) and the resulting solution was mixed with an aqueous solution (20 ml) of Na(sac) \cdot 2H₂O (0.24 g, 1 mmol) at room temperature. The resulting solution was kept in darkness at room temperature and colorless single crystals of [Ag₂(sac)₂ (pyet)₂] were obtained after two days. Yield: 82%. d.p. 127 °C. *Anal.* Calc. for C₂₈H₂₆N₄O₈S₂ Ag₂: C, 40.7; H, 3.2; N, 6.8; S, 7.8. Found: C, 40.5; H, 3.3; N, 6.10; S, 7.5%.

The following method was used for the preparation of $[Ag_4(sac)_4(pypr)_2]$. Solid Na(sac) · 2H₂O (0.24 g, 1 mmol) was added to a solution (40 ml) of AgNO₃ (0.17 g, 1 mmol) in a water and isopropanol mixture (1:1, v:v) and this resulted in the formation of a white precipitate, which was dissolved by the addition of pypr (0.14g, 1 mmol) to the reaction medium. After a week at room temperature, colourless crystals of $[Ag_4(sac)_4(pypr)_2]$ were formed. Yield: 25%. d.p. 132 °C. *Anal.* Calc. for C₄₄H₃₈N₆O₁₄S₄Ag₄: C, 36.8; H, 2.7; N, 5.9; S, 8.9. Found: C, 36.5; H, 2.8; N, 5.8; S, 9.0%.

2.3. Physical measurements

IR spectra were recorded a Jasco FT-IR-430 spectrophotometer as KBr pellets in the frequency range 4000– 300 cm⁻¹. The elemental analyses (C, H, N and S contents) were determined on a Vario EL Elemental Analyser. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample of 5–10 mg was used.

2.4. X-ray structure determination

Intensity data for $[Ag_2(sac)_2(pyet)_2]$ and $[Ag_4(sac)_4(pypr)_2]$ were collected using Bruker SMART1000 CCD and Enraf Nonius KappaCCD area diffractometers with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 133(2) and 120(2) K, respectively. The structures were solved with SHELXS 97 and refined using SHELX 97 [11]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, except the hydroxyl H atoms in [Ag_2(sac)_2(pyet)_2], were placed in idealised locations and refined by riding on their carrier atoms, whereas the hydroxyl hydrogen atoms of

Table 1

Crystallographic data for [Ag₂(sac)₂(pyet)₂] and [Ag₄(sac)₄(pypr)₂]

Compounds	[Ag ₂ (sac) ₂ (pyet) ₂]	$[Ag_4(sac)_4(pypr)_2]$
Empirical formula	$C_{28}H_{26}N_4O_8S_2Ag_2$	$C_{44}H_{38}N_6O_{14}S_4Ag_4$
Formula weight	826.38	1434.52
<i>T</i> (K)	133(2)	120(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	8.1254(6)	7.9499(2)
b (Å)	8.9300(6)	9.7924(3)
<i>c</i> (Å)	10.1782(6)	30.5148(8)
α (°)	87.327(3)	86.1339(8)
β (°)	74.734(3)	88.4027(10)
γ (°)	89.735(3)	78.4552(10)
$V(\text{\AA}^3)$	711.67(8)	2321.93(11)
Ζ	1	2
$D_{\rm c} ({\rm g/cm^3})$	1.928	2.052
$\mu (\mathrm{mm}^{-1})$	1.582	1.918
F(0 0 0) 412	1416	
θ range (°)	2.08-30.03	2.92-27.50
Index range (h, k, l)	-11/11,	-10/10,
	-12/12,	-12/12,
	-14/14	-39/39
Reflections collected	14 105	40 039
Independent reflections	4145	10 637
Maximum and minimum transmission	0.801 and 0.684	0.831 and 0.678
Data/restraints/parameters	4145/0/203	10 637/6/649
Goodness-of-fit on F^2	1.073	1.210
$R_1 \left[I > 2\sigma(I) \right]$	0.0189	0.0894
R_2 and wR_2 indices	0.0203 and 0.0500	0.0999 and 0.2394
(all data)		
Largest difference	0.623 and -0.499	3.138 and -1.512
peak and hole (e $Å^{-3}$)		

695

 $[Ag_2(sac)_2 (pyet)_2]$ were refined freely. The molecular plots were prepared by using ORTEPIII [12]. The details of data collection, refinement and crystallographic parameters are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

The mixed-ligand silver (I) complexes of sac with pyet and pypr were prepared by the direct reaction of silver (I), sac and pyet or pypr in solution. The composition of the complexes was determined by elemental and TG analyses. The binuclear complex was obtained in a high yield over 80%, whereas the yield of the tetranuclear complex was relatively low (25%). Although no other complex was isolated from the same reaction solution of the tetranuclear complex, the low yield of the complex may be due to the presence of other species with very high solubility. The elemental analyses were consistent with their proposed formulae. Both complexes are insoluble in warm H₂O and common alcohols such as methanol or ethanol, but soluble in warm H₂O-alcohol mixtures. Both complexes are non-hygroscopic and light-stable at room temperature. $[Ag_2(sac)_2(pyet)_2]$ does not melt, but decomposes at 127 °C, whereas [Ag₄ $(sac)_4(pypr)_2$ melts with decomposition at 132 °C.

3.2. IR spectra

The most significant absorption bands in the IR spectra of the title complexes together with their assignments are given in Table 2. The position of the bands in the spectra of both complexes is similar. The strong and broad bands in the 3330–3350 cm⁻¹ range are attributed to the v(OH) vibrations of the pyet and pypr ligands. The relatively weak bands at 2900–3070 cm⁻¹ are due

Table 2						
Selected	IR	spectroscopic	data ^a	for	$[Ag_2(sac)_2(pyet)_2]$	and
[Ag ₄ (sac),	(nvn	r)2]				

	21	
Assignment	[Ag ₂ (sac) ₂ (pyet) ₂]	[Ag ₄ (sac) ₄ (pypr) ₂]
v(OH)	3327s, b	3347s, b
v(CH)	3066w, 2931vw	3040w, 2920vw
v(CO)	1649vs, 1622sh	1651vs, 1626sh
v(CC)	1587vs	1583vs
v(CC)	1458m	1458vs
$v_{\rm sym}(\rm CNS)$	1331s	1336s
$v_{asym}(SO_2)$	1288vs, 1257s	1288vs, 1271vs, 1250vs
$v_{\rm sym}(\rm SO_2)$	1151vs	1155vs
v _{asym} (CNS)	966vs	970vs, 953vs
v(CCC)	773m, 748s	773m, 744s
γ(CH) (py)	676m	675s

b, broad; vw, very weak; w, weak; vs, very strong; s, strong; m, medium and sh, shoulder.

^a Frequencies in cm⁻¹.

to the v(CH) vibrations. The absorption band of the carbonyl group of sac in $[Ag_2(sac)_2(pyet)_2]$ appears at ca. 1649 cm^{-1} as a very strong, single band. The frequency of the carbonyl group is characteristic of N-coordinated sac ligands as reported for Na[Ag(sac)] [9] and Na(sac). 2H₂O [13]. However, the C=O bands in [Ag₄(sac)₄- $(pypr)_2$ are observed at 1651 and 1626 cm⁻¹ as two distinct and strong bands, indicating the different interactions of the sac ligands. The higher absorption band is due to an N-bonded sac in which its carbonyl group remains uncoordinated, whereas the band at lower frequency shows the coordination of the sac ligand through the carbonyl group, shifting by ca. 25 cm^{-1} compared to the higher band. This shift is in agreement with the participation of the carbonyl oxygen in metal bonding as also observed in the IR spectrum of [Ag(sac)] [14]. The absorption bands at ca. 1580 and 1460 cm⁻ correspond to the ring v(CC) vibrations. The stretching vibrations of $v_{asym.}(SO_2)$ and $v_{sym.}(SO_2)$ occur characteristically at ca. 1290 and 1150 cm⁻¹, respectively. In both complexes, the asymmetric stretching band at around 1280 cm^{-1} are found to split into two or three bands, although the S-O distances in both complexes are almost identical. Additional peaks at ca. 1330 and 970 cm⁻¹ are attributed to the symmetric and asymmetric stretching modes of the CNS moiety of the sac ligands, respectively. The N-coordination of the py ligands is confirmed by the absorption bands at around 675 cm⁻¹ due to $\gamma(py)$ [15].

3.3. Thermal behaviour

The thermal decomposition pathways of the title complexes were followed up to 600 °C in a static atmosphere of air. $[Ag_2(sac)_2(pyet)_2]$ is stable up to 127 °C and then begins to decompose in three stages. Elimination of the pyet ligand occurs in the first stage of decomposition between 127 and 240 °C with three endothermic effects at 150, 189 and 213 °C. The experimental mass loss of 29.5% agrees well with the calculated mass loss of 29.8%. The decomposition of the sac moiety occurs in the second and third stages in the temperature range 250–517 °C with two violently exothermic DTA peaks at 370 and 464 °C (mass loss: found 44.5%, calcd. 44.1%). As well as microanalyses, the mass loss calculations suggest that the residue left as a final decomposition product is metallic silver. Total mass loss is 74.0% and the final residue consisting mainly of silver forms 26.0% of the total mass (calcd. 26.1%).

 $[Ag_4(sac)_4(pypr)_2]$ follows a different decomposition path compared to that of the dimeric complex. It begins to decompose with melting at 132 °C. The first decomposition stage between 132 and 231 °C corresponds to the endothermic removal of two pypr ligands with a mass loss of 19.4% (calcd. 19.1%). In the next stages, the exothermic degradation of four sac ligands occurs in the 235–528 °C range with a small and two sharp exothermic DTA peaks at 256, 435 and 489 °C, and results in the formation of silver metal as the end product. The experimental total mass loss value of 70.5% is consistent with the calculated value 69.9%.

3.4. Description of the crystal structure of $[Ag_2(sac)_2(pyet)_2]$

A molecular view of $[Ag_2(sac)_2(pyet)_2]$ with the atom numbering scheme is shown in Fig. 1. The selected bond lengths and angles together with the hydrogen bonding geometry are given in Table 3. The complex crystallizes in the triclinic space group $P\overline{1}$. The structure consists of individual molecules of dinuclear $[Ag_2(sac)_2(pyet)_2]$ units formed from doubly bridged monomeric $[Ag_2(sac)_2(pyet)]$ units joined through the sulfonyl oxygen atoms of the sac ligands (Fig. 1). Each silver (I) centre is three coordinated by an *N*-bonded sac ligand, an *N*-bonded pyet ligand and the bridging sulfonyl oxygen



Fig. 1. Dimeric molecular unit in $[Ag_2(sac)_2(pyet)_2]$ with the atom labelling scheme and 50% thermal ellipsoids (arbitrary spheres for the H atoms). Symmetry code: (i) = -x, 2 - y, -z.

Table 3 Selected geometrical data for $[Ag_2(sac)_2(pyet)_2]^a$					
Bond lengths (Å)	and angles (°)				
Ag1–N1	2.1753(11)	N1–Ag	1–N2	159.14(4)	
Ag1–N2	2.1444(12)	N1–Ag	96.11(4) 104.75(4)		
Ag1–O2 ⁱ	2.6454(10)	N2–Ag			
$D – H \cdots A$	d(D–H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)	
Hydrogen bonds					
O17–H17···O1 ⁱⁱ	0.82(2)	2.02(3)	2.8083(17)	163(2)	
$C12H12 \cdots O17^{ii}$	0.95	2.55	3.4133(19)	150	
<u>C16– H16B· · · O21</u>	ⁱⁱⁱ 0.99	2.43	3.4124(16)	172	

^a Symmetry operations: (i) -x, 2 - y, -z; (ii) x, y - 1, z; (ii) 1 - x,

atom of sac in the adjacent $[Ag(sac)_2(pyet)]$ unit, exhibiting a distorted T-shaped AgN₂O coordination environment. In the dimeric unit, there is an eight-membered chelate ring with an Ag···Ag separation of 5.205 Å, indicating the absence of any interaction between two silver centres. We have previously observed that the pyet ligand behaves as a bidentate donor via the N and hydroxyl O atoms to other divalent transition metals [16–18]. Here, it acts a monodentate ligand through the N atom and the hydroxyl O atom remains uncoordinated.

The Ag–N_{sac} and Ag–N_{pyet} bond distances are similar, being 2.1753(11) and 2.1444(12) Å, respectively. The Ag–N_{sac} bond distance is similar to the corresponding values found in [Ag(sac)] [2.16 Å] [7], Na[Ag(sac)] [2.1405(11)] and 2.1570(11) Å] [9], but differs from the bond values reported for [Ag(sac)(PPh₃)₂] [2.285(8) Å] [8] and [Ag₂(μ -sac)₂(μ -hep)₂]_n [2.084(2) Å] [10]. The bridging Ag–O_{sulfonyl} bond distance of 2.6454(10) Å is comparable to that of Na[Ag(sac)] [2.6390(10) Å] [9], but significantly longer than the corresponding bond in [Ag(sac)] (2.45 Å) [7].

The sac ligand is essentially planar with a root-meansquare (rms) deviation of the non-hydrogen atoms (excluding the sulfonyl O atoms) from the best leastsquares plane of 0.03 Å and the pyet ligand is also planar with an rms deviation of 0.004 Å, but C17 and O17 atoms deviate by 1.375(2) and 2.241(2) Å, respectively, from the best pyet plane. The sac and pyet ligands coordinate to silver (I) in an approximately linear fashion with an N–Ag–N angle of 159.14(5)°. The dihedral angle between the planes of sac and pyet is $5.65(6)^{\circ}$, showing the approximately coplanar arrangement of their ring systems.

The individual $[Ag_2(sac)_2(pyet)_2]$ molecules are linked by strong hydrogen bonds between the hydrogen of the hydroxyl group and the uncoordinated sulfonyl O atom of the sac ligands in the neighbouring units, forming a one-dimensional chain running parallel to the *b*-axis (see Fig. 2(a)). The one-dimensional hydrogen bonded chains are further linked by non-conventional intermolecular C-H···O hydrogen bonds and $\pi(sac)-\pi(pyet)$ stacking interactions [Cg···Cg = 3.75(7) Å] as shown in Fig. 2(b).

3.5. Description of the crystal structure of $[Ag_4(sac)_4(pypr)_2]$

The molecular structure of the tetranuclear silver (I) complex $[Ag_4(sac)_4(pypr)_2]$ with the atom labelling is shown in Fig. 3. The selected bond lengths and angles are given in Table 4. The compound crystallizes in the triclinic space group $P\bar{1}$ and has two tetrameric molecules in its asymmetric unit with a similar conformation. The structure consists of isolated molecules of $[Ag_4(sac)_4(pypr)_2]$, which are built up from the bridging of



Fig. 2. (a) A fragment of the hydrogen bonded one-dimensional chain of $[Ag_2(sac)_2(pyet)_2]$. Symmetry code: i = -x, -y, -z. (b) Projection of the structure of $[Ag_2(sac)_2(pyet)_2]$ on the *ac* plane, showing $\pi(sac)-\pi$ (pyet) interactions. The phenyl and ethylene H atoms are removed for clarity.

the central $[Ag_2(sac)_2]$ unit with two [Ag(sac)(pypr)]units through the sulfonyl oxygen atoms of the sac ligands. $[Ag_4(sac)_4(pypr)_2]$ exhibits two different silver centres. The two silver (I) ions (Ag1 and its symmetryequivalent partner Ag1ⁱ) in the centre exhibit a T-shaped planar AgNO₂ geometry with three sac ligands, while

the two outer silver (I) ions (Ag2 and Ag2¹) are coordinated by a sac ligand and a pypr ligand in a near linear AgN₂ geometry $[N2-Ag2-N3 = 168.6(4)^{\circ}]$. The sac ligands in the central $[Ag_2(sac)_2]$ unit act as a bidentate chelating ligands via the N and carbonyl O atoms forming an roughly planar eight-membered chelate ring. The central Ag1 pair of silver atoms appear to be interacting based on the Ag–Agⁱ (i = 1 - x, 1 - y, -z) distance of 2.8480(13) Å, while Ag2 has no metal neighbours within 5 Å. The separation of the two central Ag3 atoms in the second asymmetric molecule of [Ag₄(sac)₄(pypr)₂] is 2.8590(13) Å. These silver-silver contacts are some 0.60 Å shorter than twice the van der Waals radius of silver (3.44 Å) and clearly indicate a strong bonding interaction between the Ag1 and the Ag3 centres in the tetranuclear complex. The Ag-Ag distances found in $[Ag_4(sac)_4(pypr)_2]$ are also much shorter than those tetranuclear reported for other silver units $[Ag_4(SPh)_4(PPh_3)_4]$ [3.1300(3) Å] [19] and $[Ag_4(tren A)_4]$ $(\min)_{3}_{2}^{4+}$ [2.929(1) and 3.1313(9) Å] [20], where SPh and tren(mim)₃ are thiolate and tris {2-2(1-methyl)imidazolyl]methyliminoethyl} amine, respectively. The significance of short silver-silver distances has been debated: Jansen reported a value of 3.30 Å as the upper limit for an Ag···Ag contact in coordination compounds [21], whereas Dance et al. [22] stated that since the linear geometry at silver (I) indicates the fulfilment of its coordination requirements, there is no bonding interaction between silver (I) centres as close to each other as 2.886 Å in [Ag(SCMeEt)₂]_n. However, we argue that there is a significant bonding interaction between the silver centres at the short distances in the present $[Ag_4(sac)_4(pypr)_2]$ complex.

The Ag– N_{sac} bond distances in $[Ag_4(sac)_4(pypr)_2]$ are similar to those reported for the related silver (I)-saccharinato complexes [7,9–11], but the terminal Ag– N_{sac}



Fig. 3. View of tetrameric unit in $[Ag_4(sac)_4(pypr)_2]$ with the atom labelling scheme and 50% thermal ellipsoids (arbitrary spheres for the H atoms). Symmetry code (i) = 1 - x, 1 - y, -z. The asymmetric unit of the complex contains two molecules and one of them was removed for clarity.

Table 4 Selected geometrical data for [Ag₄(sac)₄(pypr)₂]^a

Bond lengths (Å)	and angles (°))			
Agl–Nl ⁱ	2.184(10)	N1–A	165.5(3) 106.2(3) 88.2(3)		
Ag1–O1	2.230(8)	N1–A			
Ag1–O5	2.431(9)	O1-Ag1-O5			
Ag2–N2	2.102(10)	N2–A	N2–Ag2–N3 N2–Ag2– O3 ⁱ		
Ag2–N3	2.140(10)	N2–A			
Ag2–O3 ⁱ	2.960(9)	N3–Ag2– O3 ⁱ		92.2(3)	
Ag1–Ag1 ⁱ	2.8480(13)				
$D - H \cdots A$	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)	
Hydrogen bonds ^b					
$O7-H1$ ··· $O10^{ii}$	0.90	1.89	2.793(14)	180	
$O14-H2 \cdot \cdot \cdot O2^i$	0.90	1.89	2.788(14)	180	
$C16H16\cdots\text{-}O14^{iii}$	0.95	2.48	3.360(17)	154	
C38–H38···O7 ^{iv}	0.95	2.20	3.127(17)	165	
C40–H40···O2 ⁱ	0.95	2.38	3.289(17)	161	

^a Symmetry operations: (i) 1 - x, 1 - y, -z; (ii) 1 - x, 1 - y, 1 - z; (iii) 1 + x, y, z; and (iv) 1 + x, y - 1, z.

^b O10, O17 and C38 and C40 atoms belongs to the second molecule in the asymmetric unit of the compound.

bond distances are noticeably longer than the corresponding bonds and the Ag-Osac bonds in the central unit. The Ag-O_{carbonyl} bond distance of 2.230(8) Å is almost identical to that observed in [Ag(sac)] [2.22 Å] [7], but slightly shorter than those found in $[Ag_2(\mu-sac)_2$ $hep)_{2n} [2.2535(11) and 2.3010(14) A] [10].$ The bridging Ag–O_{sulfonvl} bond distance of 2.431(9) A is similar to the equivalent value observed in [Ag(sac)] (2.45 Å) [7], but is significantly shorter than the 2.6390(10) A found in Na[Ag(sac)] [9]. Furthermore, there is a weaker interaction between the sulfonyl O atoms of the sac ligands in the central unit and the silver (I) centres at the terminal units, yielding a Ag-Osulfonyl bond distance of 2.960(9) Å and probably suggesting the "semi-coordination" of the sulfonyl group of sac to silver (I). The Ag-N_{pvpr} bond distance is 2.140(10) A. Similarly, the hydroxyl group of pypr is uncoordinated in $[Ag_4(sac)_4(pypr)_2]$ in contrast to the bidentate coordination behaviour in the presence of divalent transition metals [23-25]. This may be explained in terms of hard and soft acids and bases. As a soft acid, silver (I) will not prefer a hard base OH for coordination.

The ring systems of sac and pypr are planar. The rms deviations from the best planes of the sac1 with N1, sac2 with N2 and pypr species are 0.010, 0.016 and 0.012 Å, respectively. The displacement of the silver (I) ions from the corresponding planes is as follows: Ag1 from sac1 = 0.356(11) Å, Ag2 from sac2 = 0.212(9) Å and Ag2 from pypr = 0.0429(19) Å. The planes of sac and pypr coordinated the terminal Ag2 atoms are roughly coplanar with a dihedral angle of $10.7(6)^{\circ}$.

The unit-cell packing of the molecules of $[Ag_4(sac)_4 (pypr)_2]$ is shown in Fig. 4. Relevant hydrogen bonds are listed in Table 4. The packing of the tetramers forms

Fig. 4. A view of the unit cell of $[Ag_4(sac)_4(pypr)_2]$ viewed along the *a* axis. It shows the packing of the tetramers to form a herringbone motif. The phenyl and ethylene H atoms are removed for clarity.

a herring-bone motif. The two molecules in the asymmetric unit of the structure are connected by strong intermolecular $O-H\cdots O$ bonds $(H\cdots O = 1.89$ Å), involving the hydroxyl H of pypr and sulfonyl O of sac. The O10, O17 and C38 and C40 atoms belongs to the second molecule in the asymmetric unit of the compound. The strong hydrogen bonds form hydrogen bonded dimers, which are further linked by $C-H\cdots O$ interactions, resulting in a layered structure. The C38–H38 \cdots O7^{iv} bond has an exceptionally short H \cdots O contact of 2.20 Å, but this may arise from unmodelled disorder of some of the carbon atoms in the py ring containing C38.

4. Supplementary material

Crystallographic data for the structures reported in the paper have been deposited at the CCDC as supplementary data, CCDC Nos. 253479 and 253480 for $[Ag_2(sac)_2(pyet)_2]$ and $[Ag_4(sac)_4(pypr)_2]$, respectively. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac. uk; http://www.ccdc.cam.ac.uk).

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