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Original article

Synthesis and antimicrobial activities of silver(I) 3-(substituted phenyl)sulfanylpropenoates

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ABSTRACT

We investigated the reactions of silver nitrate with 3-(substituted phenyl)-2-sulfanylpropenoic acids H_2L [L = xspa, where spa = 2-sulfanylpropenoato and x ∈ {Clp = 3-(2-chlorophenyl)-, -*o*-mp = 3-(2-methoxyphenyl)-, -*o*-hp = 3-(2-hydroxyphenyl)-, -*p*-hp = 3-(4-hydroxyphenyl)-, diBr-*o*-hp = 3-(3,5-dibromo-2-hydroxyphenyl)-}] in 1:1 and 2:1 molar ratios. The 1:1 reactions gave compounds of type [Ag(HL)], which reacted with NaOH to afford $Na[Ag(L)]\cdot xH_2O$ ($x = 1$ or 2) and with diisopropylamine to afford [HQ][Ag(L)] (HQ = diisopropylammonium). The 2:1 reactions gave products of type $[Ag_2(L)]$. All the new compounds were isolated and characterized by IR spectroscopy, and all except the 2:1 adducts (which were insoluble) were studied by ^1H and ^{13}C NMR spectroscopy; ESI-MS spectrometry was also used for [HQ][Ag(L)] and $Na[Ag(L)]\cdot xH_2O$, and the crystal structures of H_2Clpspa and [HQ][Ag(Clpspa)] were determined by X-ray diffractometry. The antimicrobial activities of the complexes against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Candida albicans*, *Pseudomonas aeruginosa* and carbapenem-resistant *P. aeruginosa* were evaluated and compared with those of Ag(I) complexes with other aryl sulfanylpropenoates or related ligands.

1. Introduction

The antibacterial effects of silver compounds have long been known, and silver nitrate and certain silver complexes are still used against local infections [1–4]. Several possible mechanisms for the antimicrobial activity of the aqueous silver(I) ion have been hypothesized [5–7], including interference with electron transport, binding to DNA, interaction with the cell membrane, and interaction with the thiol groups of vital enzymes. Resistance to Ag(I) ion has also been reported [2,4,8]. The search for new complexes and materials allowing biocidal Ag^+ ions to be delivered with increased efficiency is currently an active research area [9,10]. Complexes with Ag–N [9,11–14] and Ag–O [15–21] bonds have exhibited a broad spectrum of antimicrobial activities, while those with Ag–S bonds [22–25] have a narrower spectrum but are highly effective against certain bacteria, yeasts and moulds.

As part of an exploration of new chemical environments for the Ag(I) ion that might make it more bioavailable [10,26] and to increase structural knowledge of silver(I) compounds [27] with a view to the inference of structure–activity relationships, in previous work [28] we prepared silver(I) complexes of several thiolated organic acids H_2L, namely 2-cyclopentylidene-2-sulfanylacetic acid (H_2cpa) and 3-(aryl)-2-sulfanylpropenoic acids H_2xspa, where spa = 2-sulfanylpropenoato and x = {p = 3-phenyl-, f = 3-(2-furyl)-, t = 3-(2-thienyl)-, py = 3-(2-pyridyl)-} (H_2pspa, H_2fspa, H_2tspa and H_2-*o*-pyspa, respectively). The complexes obtained were of the types [Ag(HL)], $[Ag_2(L)]$, $Na[Ag(L)]\cdot H_2O$ and [HQ][Ag(L)] (HQ = diisopropylammonium). [HQ][Ag(pspa)] was found to be composed of HQ^+ cations and tetrameric $[Ag_4(pspa)_4]^{4-}$ units containing a central Ag_4S_4 ring, and thus augmented a small group of oligomeric Ag(I) complexes that includes $[Ag(Hmna)]_6$ [25], $K_{12}[Ag_8(mba)_{10}]\cdot 12H_2O$ [29], $Na_{12}[Ag_8(mba)_{10}]\cdot 5H_2O\cdot 2MeOH$ [29], $\{[Ag_6(Hmna)_4(mna)_2][Et_3NH](DMSO)_2\}$ [30] and $[Ag(mna)_6]^{6-}\cdot 4Na^+\cdot 2[(HOCH_2)_3CNH_3]^+\cdot 10H_2O$ [31], where H_2mna = 2-mercaptonicotinic acid and H_2mba = 2-mercaptobenzoic acid.

Since the biological activities of metal complexes with ligands containing a phenyl ring are known to be influenced by the substituents on the ring [32–35], we decided to expand our previous study to embrace the ligands H_2L shown in Scheme 1. This paper describes the synthesis, characterization and antimicrobial activities of their silver(I) complexes of types [Ag(HL)], $[Ag_2(L)]$, [HQ][Ag(L)] (HQ = diisopropylammonium) and $Na[Ag(L)]\cdot xH_2O$

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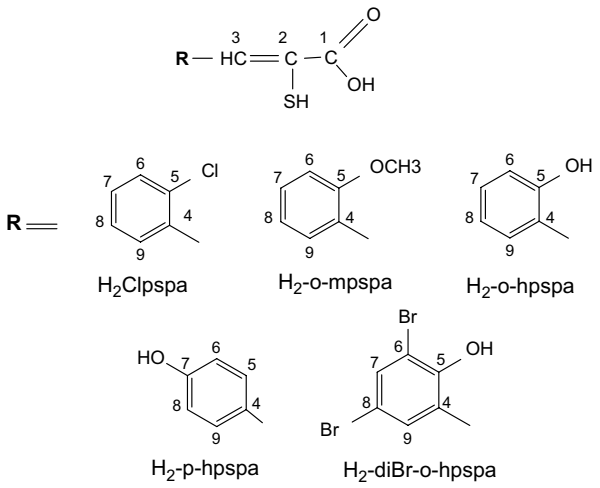

Scheme 1.

($x = 1$, 2), and the crystal structures of H_2Clpspa and of [HQ][Ag(Clpspa)], the last one composed of HQ^+ cations and $[Ag_4(Clpspa)_4]^{4-}$ anions.

2. Experimental

2.1. Materials and methods

2-Chlorobenzaldehyde, 2-methoxybenzaldehyde, 2-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 3,5-dibromo-2-hydroxybenzaldehyde, rhodanine and triethylamine (all from Aldrich), silver nitrate (Prolabo), Ag_2O and diisopropylamine (Merck), and NaOH (Probus) were all used as supplied. 3-(Aryl)-2-sulfanylpropenoic acids were prepared by condensation of the appropriate aldehyde with rhodanine [36], followed by hydrolysis in an alkaline medium and acidification with aqueous HCl [37]; specific experimental conditions are described in Ref. 38 for H_2Clpspa, H_2-*o*-mpspa and H_2-diBr-*o*-hpspa, and in Ref. 39 for H_2-*o*-hpspa.

Elemental analyses were performed with a Fisons 1108 micro-analyser. Melting points were determined with a Büchi apparatus and are uncorrected. IR spectra were recorded from KBr pellets or Nujol mulls on a Bruker IFS66V FT-IR spectrophotometer and are reported in Section 2.4 using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. ^{1}H, ^{13}C and DEPT NMR spectra were recorded in DMSO-d_6 at room temperature on a Bruker AMX 300 spectrometer operating at 300.14 MHz (^{1}H) and 75.40 MHz (^{13}C), using 5 mm o.d. tubes; chemical shifts are reported relative to TMS using the solvent signal (δ ^{1}H = 2.50 ppm; δ ^{13}C = 39.50 ppm) as reference. Electrospray mass spectra (ESI-MS) were obtained in negative ion mode on a Bruker Microtof using methanol as solvent, a capillary voltage of 4500 V and a cone voltage of 10 V.

2.2. X-ray crystallography

Single crystals of H_2Clpspa and [HQ][Ag(Clpspa)] (**11**) were mounted on glass fibres in a Bruker Smart CCD automatic diffractometer. Data were collected using Mo Kα radiation ($\lambda = 0.71073$ Å). Corrections for Lorentz effects, polarization [40] and absorption [41] were made. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELX-97 [42]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at their ideal positions and refined as riders. Graphics were produced with PLATON and MERCURY [43]. Since the crystal of H_2Clpspa was only weakly diffracting, a large number of "unobserved" reflections were used in refining its structure, giving rise to rather large values of R_1, wR_2 and the maximum residual electron density. However, the overall structure and packing of this ligand are clear, and have accordingly been included in the discussion for comparative purposes.

The crystal data, experimental details and refinement results are summarized in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC No. 681145 (H_2Clpspa) and CCDC No. 681146 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail deposit@ccdc.com.as.uk).

2.3. Antimicrobial activity

Antibacterial activity was initially assayed by Müller–Hinton agar diffusion methods. Compounds **1**–**5** were suspended in water containing 0.1% of DMSO, the ligands and compounds **11**–**15** were dissolved in ethanol, and compounds **16**–**20** were dissolved in water. Paper discs of 5 mm in diameter were loaded with 20 μL of a 2 mg/cm^3 solution or suspension of the substance to be tested, control discs were loaded with solvent alone, and the discs were then placed on dishes of Müller–Hinton agar inoculated with *Staphylococcus aureus* (ATCC29213), *Bacillus subtilis* (ATCC6633), *Escherichia coli* (ATCC25922), *Pseudomonas aeruginosa* (ATCC27853), a carbapenem-resistant strain of *P. aeruginosa* (hereinafter "resistant *P. aeruginosa*"), and *Candida albicans* (ATCC10231). After 24 hours' incubation at 37 °C, the diameters of the bacterial growth inhibition zones were measured. All assays were carried out in duplicate. For products showing activity, serial dilutions in Müller–Hinton broth were used as described in the literature [44] to determine minimum inhibitory concentration (MIC), defined as the lowest concentration of the substance under test that inhibits the visible growth of the test organism when the latter is at optimal concentration.

2.4. Synthesis

2.4.1. Complexes of type [Ag(HL)]

Method A (compounds **1**–**5**). An equimolar solution of $AgNO_3$ and Et_3N in acetonitrile was added to a solution of the appropriate sulfanylcarboxylic acid in ethanol to form a mixture with an $AgNO_3$:ligand molar ratio of 1:1. The mixture was stirred at room temperature for 1 h, and the resulting solid was filtered out, washed

Table 1
Crystal data for H_2Clpspa and [HQ][Ag(Clpspa)] (**11**)

Compound	H_2Clpspa	[HQ][Ag(Clpspa)] (**11**)
Empirical formula	$C_9H_7ClO_2S$	$C_{60}H_{84}Ag_4Cl_4N_4O_8S_4$
M	214.66	1690.83
T/K	293(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*
a/Å	3.9264(10)	12.811(4)
b/Å	17.826(4)	20.090(6)
c/Å	13.237(3)	15.305(5)
β/°	923.44(4)	111.313(6)
V/Å^3	3023.0(19)	3669.6(19)
Z	4	2
D_c/Mg m^{-3}	1.544	1.530
μ/mm^{-1}	0.599	1.360
Crystal size/mm^3	0.34 × 0.26 × 0.19	0.33 × 0.30 × 0.14
θ Range for data collection/°	1.92–28.04	1.75–28.09
Index ranges (*h*, *k*, *l*)	−5, 4; −23, 21; −16, 17	−16, 16; −26, 24; −20, 16
Reflections collected	5984	24025
Unique reflections, *R*	2203 [*R*(int) = 0.1490]	8840 [*R*(int) = 0.1341]
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.1225, 0.3067	0.0521, 0.0845
Final *R* indices (all data)	0.1951, 0.3451	0.2047, 0.1127

with ethanol, water and ether, and dried in vacuo. *Method B* (compounds **4** and **5**). An aqueous suspension of Ag_2O was added to a solution of the appropriate sulfanylcarboxylic acid in aqueous NaOH to form a mixture with an Ag_2O:NaOH:ligand molar ratio of 1:4:2. The mixture was stirred at room temperature for 24 h, passed through Whatman No. 42 paper, acidified with 0.5 M H_2SO_4, stirred for a further 20 min, and the resulting solid was filtered or centrifuged out, washed with ethanol, water and ether, and dried in vacuo.

*2.4.1.1. [Ag(HClpspa)] (**1**).* H_2Clpspa (0.15 g, 0.77 mmol), $AgNO_3$ (0.12 g, 0.7 mmol), ethanol (15 cm^3), Et_3N (0.089 cm^3, 0.74 mmol), CH_3CN (8 cm^3). Yield 70%. Beige solid, mp 210 °C. Anal. Found: C 33.5, H 1.7, S 9.7%. Calcd for $C_9H_6O_2SClAg$: C 33.6, H 1.9, S 10.0%. IR (cm^{-1}): 1675 vs, ν(C=O); 1419 m, δ(OH); 1266 s, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ - (br s, 1H, C(1)OH), 7.88 (s, 1H, C(3)H), 7.44 (dd, 1H, C(6)H), 7.30 (m, 2H, C(7)H and C(8)H), 8.41 (dd, 1H, C(9)H); ^{13}C, δ 170.3 C(1), - C(2), 134.3 C(3), 133.5 C(4), 133.4 C(5), 130.2 C(6), 131.6 C(7), 126.9 C(8), 129.6 C(9).

*2.4.1.2. [Ag(H-o-mpspa)] (**2**).* H_2-*o*-mpspa (0.10 g, 0.48 mmol), $AgNO_3$ (0.08 g, 0.48 mmol), ethanol (10 cm^3), Et_3N (0.066 cm^3, 0.48 mmol), CH_3CN (5 cm^3). Yield 78%. Pale yellow solid, mp 150 °C (dec.). Anal. Found: C 37.4, H 2.7, S 9.9%. Calcd for $C_{10}H_9O_3SAg$: C 37.9, H 2.9, S 10.1%. IR and Raman (R) (cm^{-1}): 1669 m, br, ν(C=O); 1384 m, δ(OH); 1246 vs, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ 12.99 (br s, 1H, C(1)OH), 8.02 (s, 1H, C(3)H), 8.49 (d, 1H, C(6)H), 6.94 (m, 2H, C(7)H and C(9)H), 7.24 (t, 1H, C(8)H), 3.77 (s, 3H, OCH_3); ^{13}C, δ 170.5 C(1), 128.4 C(2), 133.3 C(3), 124.3 C(4), 157.1 C(5), 110.7 C(6), 130.1 C(7), 119.6 C(8), 129.8 C(9), 55.4 C(OCH_3).

*2.4.1.3. [Ag(H-o-hpspa)] (**3**).* H_2-*o*-hpspa (0.10 g, 0.51 mmol), $AgNO_3$ (0.086 g, 0.51 mmol), ethanol (10 cm^3), Et_3N (0.07 cm^3, 0.51 mmol), CH_3CN (5 cm^3). Yield 60%. Orange solid, mp 150 °C (dec.). Anal. Found: C 35.9, H 2.1, S 10.8%. Calcd for $C_9H_7O_3SAg$: C 35.7, H 2.3, S 10.6%. IR (cm^{-1}): 1708 vs, 1678 vs, ν(C=O); 1446 s, δ(OH); 1248 s, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ 12.97 (br s, 1H, C(1)OH), 7.97 (s, 1H, C(3)H), 8.51 (s, 1H, C(5)OH), 6.78 (m, 2H, C(6)H and C(8)H), 7.02 (st, 1H, C(7)H), - (d, 1H, C(9)H); ^{13}C, δ 171.6 C(1), 123.8 C(2), 128.9 C(3), 131.2 C(4), 155.7 C(5), 115.1 C(6), 129.9 C(7), 118.2 C(8), 130.6 C(9).

*2.4.1.4. [Ag(H-p-hpspa)] (**4**) (by* Method B*).* H_2-*p*-hpspa (0.17 g, 0.87 mmol), Ag_2O (0.1 g, 0.43 mmol), ethanol (15 cm^3), NaOH (0.07 g, 0.174 mmol), H_2O (5 cm^3), 0.5 M H_2SO_4 (1.72 cm^3, 087 mmol). Yield 60%. Yellow solid, mp 153 °C (dec.). Anal. Found: C 35.4, H 2.4, S 10.6%. Calcd for $C_9H_7O_3SAg$: C 35.7, H 2.3, S 10.6%. IR (cm^{-1}): 1657 s, ν(C=O); 1437 m, δ(OH); 1240 vs, br, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ 12.49 (br s, 1H, C(1)OH), 7.75 (s, 1H, C(3)H), 8.06 (d, 2H, C(5)H, C(9)H), 6.78 (d, 2H, C(6)H, C(8)H), 9.86 (s, 1H, C(7)OH); ^{13}C, δ 171.4 C(1), 124.6 C(2), 139.7 C(3), 127.3 C(4), 133.3 C(5) and C(9), 115.4 C(6) and C(8), 158.5 C(7).

*2.4.1.5. [Ag(H-diBr-o-hpspa)] (**5**) (by* Method B*).* H_2diBr-*o*-hpspa (0.15 g, 0.43 mmol), Ag_2O (0.05 g, 0.21 mmol), ethanol (15 cm^3), NaOH (0.04 g, 0.86 mmol), H_2O (5 cm^3), 0.5 M H_2SO_4 (0.84 cm^3, 0.43 mmol). Yield 72%. Dark orange solid, mp 150 °C (dec.). Anal. Found: C 23.6, H 1.0, S 6.9%. Calcd for $C_9H_5O_3SBr_2Ag$: C 23.4, H 1.0, S 7.0%. IR (cm^{-1}): 1663 vs, ν(C=O); 1407 m, δ(OH); 1257 vs, ν(C–O). NMR (DMSO-d_6): ^{1}H, δ - (br s, 1H, C(1)OH), 8.64 (s, 1H, C(3)H), 9.85 (br s, 1H, C(5)OH), 7.89 (s, 1H, C(7)H), 7.62 (d, 1H, C(9)H); ^{13}C, δ 170.4 C(1), 128.3 C(2), 131.5 C(3), 132.7 C(4), 151.4 C(5), 112.6 C(6), 133.9 C(7), 110.6 C(8), 131.1 C(9).

2.4.2. Complexes of type [Ag_2(L)]

Complexes **6**–**10** were prepared by adding a solution of $AgNO_3$ in acetonitrile to a solution of the appropriate sulfanylcarboxylic acid and Et_3N in ethanol to form a mixture with an $AgNO_3$:ligand:Et_3N molar ratio of 2:1:2 that was stirred for 1 h. The resulting solid was filtered out, washed with water, ethanol and ether, and dried in vacuo.

*2.4.2.1. [Ag_2(Clpspa)] (**6**).* H_2Clpspa (0.10 g, 0.47 mmol), $AgNO_3$ (0.16 g, 0.94 mmol), ethanol (10 cm^3), Et_3N (0.13 cm^3, 0.94 mmol), CH_3CN (8 cm_3). Yield 88%. Dark yellow solid, mp 165 °C (dec.). Anal. Found: C 25.3, H 1.3, S 7.5%. Calcd for $C_9H_5O_2SClAg_2$: C 25.2, H 1.2, S 7.5%. IR (cm^{-1}): 1563 vs, ν_{as}(COO^-); 1356 s, ν_{sym}(COO^-).

*2.4.2.2. [Ag_2(-o-mpspa)] (**7**).* H_2-*o*-mpspa (0.10 g, 0.48 mmol), $AgNO_3$ (0.16 g, 0.94 mmol), ethanol (10 cm^3), Et_3N (0.14 cm^3, 0.94 mmol), CH_3CN (8 cm^3). Yield 78%. Brown solid, mp 160 °C (dec.). Anal. Found: C 28.1, H 1.8, S 7.4%. Calcd for $C_{10}H_8O_3SAg_2$: C 28.3, H 1.9, S 7.6%. IR (cm^{-1}): 1556 vs, ν_{as}(COO^-); 1354 s, ν_{sym}(COO^-).

*2.4.2.3. [Ag_2(-o-hpspa)] (**8**).* H_2-*o*-hpspa (0.10 g, 0.51 mmol), $AgNO_3$ (0.17 g, 0.102 mmol), ethanol (10 cm^3), Et_3N (0.15 cm^3, 0.102 mmol), CH_3CN (8 cm^3). Yield 89%. Orange solid, mp 160 °C (dec.). Anal. Found: C 26.4, H 1.6, S 7.6%. Calcd for $C_9H_6O_3SAg_2$: C 26.4, H 1.5, S 7.8%. IR (cm^{-1}): 1553 vs, ν_{as}(COO^-); 1356 vs, ν_{sym}(COO^-).

*2.4.2.4. [Ag_2(-p-hpspa)] (**9**).* H_2-*p*-hpspa (0.10 g, 0.51 mmol), $AgNO_3$ (0.17 g, 0.102 mmol), ethanol (10 cm^3), Et_3N (0.15 cm^3, 0.102 mmol), CH_3CN (8 cm^3). Yield 96%. Brown solid, mp 172 °C. Anal. Found: C 26.3, H 1.6, S 7.5%. Calcd for $C_9H_6O_3SAg_2$: C 26.4, H 1.5, S 7.8%. IR (cm^{-1}): 1544 vs, ν_{as}(COO^-); 1346 vs, ν_{sym}(COO^-).

*2.4.2.5. [Ag_2(-diBr-o-hpspa)] (**10**).* H_2diBr-*o*-hspspa (0.10 g, 0.28 mmol), $AgNO_3$ (0.1 g, 0.56 mmol), ethanol (10 cm^3), Et_3N (0.08 cm^3, 0.56 mmol), CH_3CN (8 cm^3). Yield 71%. Brown solid, mp 160 °C (dec.). Anal. Found: C 18.9, H 0.7, S 5.9%. Calcd for $C_9H_4O_3SBr_2Ag_2$: C 19.0, H 0.7, S 5.7%. IR (cm^{-1}): 1563 vs, ν_{as}(COO^-); 1350 vs, ν_{sym}(COO^-).

2.4.3. Complexes of type [HQ][Ag(L)]

Complexes **11**–**15** were prepared by adding diisopropylamine to a suspension of the appropriate [Ag(HL)] complex in ethanol. The mixture was stirred at room temperature for 24 h, the resulting solid was filtered out and dried in vacuo, and the ethanol was evaporated from the filtrate at room temperature.

*2.4.3.1. [HQ][Ag(Clpspa)] (**11**).* [Ag(HClpspa)] (0.05 g, 0.15 mmol), diisopropylamine (0.02 cm^3, 0.15 mmol), ethanol (5 cm^3). Yield 92%. White solid, mp 184 °C. Anal. Found: C 42.1, H 4.9, S 7.3, N 3.3%. Calcd for $C_{15}H_{21}O_2SNClAg$: C 42.6, H 5.0, S 7.6, N 3.3%. IR (cm^{-1}): 1620 vs, $\nu(NH_2^+)$; 1552 vs, ν_{as}(COO^-); 1348 vs, ν_{sym}(COO^-). NMR (DMSO-d_6): ^{1}H, δ 7.66 (s, 1H, C(3)H), 7.40 (d, 1H, C(6)H), 7.18 (t, 1H, C(7)H), 7.30 (t, 1H, C(8)H), 8.52 (d, 1H, C(9)H), 1.21 (d, 12H, [Q]CH_3), 3.30 (m, 2H, [Q]CH), 9.18 (s, 2H, [Q]NH_2^+); ^{13}C, δ 170.5 C(1), - C(2), 132.4 C(3), 135.8 C(4), 132.7 C(5), 128.7 C(6), 130.9 C(7), 126.0 C(8), 127.9 C(9), 45.6 CH[HQ], 18.7 CH_3[HQ]. ESI-MS (−): *m*/*z* 642 (0.5%, Ag_2(HClpspa)(Clpspa)), 857 (6.7%, Ag_2(HClpspa)$_3$). Single crystals were grown from MeOH/DMSO by slow evaporation of the solvent.

*2.4.3.2. [HQ][Ag(-o-mpspa)] (**12**).* [Ag(H-*o*-mpspa)] (0.07 g, 0.20 mmol), diisopropylamine (0.03 cm^3, 0.20 mmol), ethanol (7 cm^3). Yield 61%. Beige solid, mp 190 °C (dec.). Anal. Found: C 45.3, H 6.0, S 7.3, N 3.2%. Calcd for $C_{16}H_{24}O_3SNAg$: C 45.9, H 5.8, S 7.7, N 3.3%. IR (cm^{-1}): 1620 vs, $\nu(NH_2^+)$; 1545 vs, ν_{as}(COO^-); 1349 vs, ν_{sym}(COO^-). NMR (DMSO-d_6): ^{1}H, δ 7.69 (s, 1H, C(3)H), 8.49 (d, 1H, C(6)H), 6.91 (m, 2H, C(7)H and C(9)H), 7.15 (t, 1H, C(8)H), 3.75 (s, 3H, OCH_3), 1.20 (d, 12H, [Q]CH_3), 3.27 (m, 2H, [Q]CH), 9.00 (s, 2H,

[Q]NH_2^+); ^{13}C, δ 171.3 C(1), 127.2 C(2), 129.9 C(3), 126.5 C(4), 156.7 C(5), 110.3 C(6), 127.7 C(7), 119.3 C(8), 125.6 C(9), 55.1 C(OCH_3), 45.5 CH[HQ], 18.9 CH_3[HQ]. ESI-MS (−): *m/z* 843 (3.4%, Ag_2(H-*o*-mpspsa)$_3$), 950 (6.0%, Ag_3(H-*o*-mpspa)$_2$(-*o*-mpspa)), 1057 (4.7%, Ag_4(H-*o*-mpspa)(-*o*-mpspa)$_2$), 1267 (17%, Ag_4(H-*o*-mpspa)$_3$(-*o*-mpspa)).

*2.4.3.3. [HQ][Ag(-o-hpspa)] (**13**).* [Ag(H-*o*-hpspa)] (0.05 g, 0.16 mmol), diisopropylamine (0.02 cm^3, 0.16 mmol), ethanol (5 cm^3). Yield 76%. Pale orange solid, mp 155 °C. Anal. Found: C 44.3, H 5.3, S 7.7, N 3.6%. Calcd for $C_{15}H_{22}O_3SNAg$: C 44.6, H 5.5, S 7.9, N 3.5%. IR (cm^{-1}): 1629 s, $\nu(NH_2^+)$; 1544 vs, $\nu_{as}(COO^-)$; 1354 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.78 (s, 1H, C(3)H), 9.35 (s, 1H, C(5)OH), 6.76 (m, 2H, C(6)H and C(8)H), 6.98 (st, 1H, C(7)H), 8.46 (d, 1H, C(9)H), 1.18 (d, 12H, [Q]CH_3), 3.25 (m, 2H, [Q]CH), 9.35 (s, 2H, [Q]NH_2^+); ^{13}C, δ 171.6 C(1), 124.9 C(2), 127.7 C(3), - C(4), 155.3 C(5), 114.8 C(6), 128.3 C(7) 117.9 C(8), 129.8 C(9), 45.6 CH[HQ], 19.0 CH_3[HQ]. ESI-MS (−): *m/z* 607 (1.6%, Ag_2(H-*o*-hpspa)(-*o*-hpspa)), 803 (2.1%, Ag_2(H-*o*-hpspa)$_3$), 908 (0.9%, Ag_3(H-*o*-hpspa)$_2$(-*o*-hpspa)), 1208 (1.0%, Ag_4(-*o*-hpspa)$_4$), 1214 (0.7%, Ag_4(H-*o*-hpspa)$_3$(-*o*-hpspa)).

*2.4.3.4. [HQ][Ag(-p-hpspa)] (**14**).* [Ag(H-*p*-hpspa)] (0.05 g, 0.16 mmol), diisopropylamine (0.02 cm^3, 0.16 mmol), ethanol (5 cm^3). Yield 60%. Pale orange solid, mp 160 °C (dec.). Anal. Found: C 44.2, H 5.3, S 7.6, N 3.3%. Calcd for $C_{15}H_{22}O_3SNAg$: C 44.6, H 5.5, S 7.9, N 3.5%. IR (cm^{-1}): 1606 vs, $\nu(NH_2^+)$; 1536 vs, $\nu_{as}(COO^-)$; 1346 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.47 (s, 1H, C(3)H), 7.89 (d, 2H, C(5)H, C(9)H), 6.70 (d, 2H, C(6)H, C(8)H), 8.90 (s, 1H, C(7)OH), 1.19 (d, 12H, [Q]CH_3), 3.25 (m, 2H, [Q]CH), 9.50 (s, 2H, [Q]NH_2^+); ^{13}C, δ 171.5 C(1), - C(2), - C(3), 128.9 C(4), 131.3 C(5) and C(9), 114.5 C(6) and C(8), 156.4 C(7), 45.6 CH[HQ], 19.0 CH_3[HQ]. ESI-MS (−): *m/z* 607 (0.9%, Ag_2(H-*p*-hpspa)(-*p*-hpspa)), 803 (4.3%, Ag_2(H-*p*-hpspa)$_3$), 908 (0.8%, Ag_3(H-*p*-hpspa)$_2$(-*p*-hpspa)), 1208 (0.7%, Ag_4(-*p*-hpspa)$_4$).

*2.4.3.5. [HQ][Ag(-diBr-o-hpspa)] (**15**).* [Ag(H-diBr-*o*-hpspa)] (0.07 g, 0.15 mmol), diisopropylamine (0.02 cm^3, 0.15 mmol), ethanol (7 cm^3), yellow solid. Yield 72%, mp 155 °C. Anal. Found: C 32.3, H 2.5, S 5.2, N 2.2%. Calcd for $C_{15}H_{20}O_3SBr_2NAg$: C 32.0, H 3.6, S 5.7, N 2.5%. IR (cm^{-1}): 1629 m, $\nu(NH_2^+)$; 1548 vs, br, $\nu_{as}(COO^-)$; 1347 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 8.48 (s, 1H, C(3)H), - (br s, 1H, C(5)OH), 7.80 (s, 1H, C(7)H), 7.39 (s, 1H, C(9)H), 1.13 (d, 12H, [Q]CH_3), 3.20 (m, 2H, [Q]CH), - (s, 2H, [Q]NH_2^+); ^{13}C, δ 172.1 C(1), - C(2), 136.3 C(3), - C(4), 157.0 C(5), 116.9 C(6), 131.8 C(7), 114.0 C(8), 130.0 C(9), 46.5 CH[HQ], 19.5 CH_3[HQ]. ESI-MS (−): *m/z* 924 (0.6%, Ag_2(H-diBr-*o*-hpspa)(diBr-*o*-hpspa)), 1277 (0.5%, Ag_2(H-diBr-*o*-hpspa)$_3$).

2.4.4. Complexes of types Na[Ag(L)]·H_2O and Na[Ag(L)]·2H_2O

Complexes **16**–**20** were prepared by adding NaOH to a suspension of the appropriate [Ag(HL)] complex in water. The mixture was stirred at room temperature for 24 h and passed through Whatman No. 42 paper, and the solvent was evaporated at room temperature.

*2.4.4.1. Na[Ag(Clpspa)]·H_2O (**16**).* [Ag(HClpspa)] (0.15 g, 0.43 mmol), NaOH (0.019 g, 0.43 mmol), H_2O (15 cm^3). Yield 75%. Pale yellow solid, mp 140 °C (dec.). Anal. Found: C 30.7, H 1.6, S 9.3%. Calcd for $C_9H_7O_3SClAgNa$: C 29.9, H 1.9, S 8.9%. IR (cm^{-1}): 1558 vs, $\nu_{as}(COO^-)$; 1365 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.65 (s, 1H, C(3)H), 7.39 (d, 1H, C(6)H), 7.19 (t, 1H, C(7)H), 7.31 (t, 1H, C(8)H), 8.54 (d, 1H, C(9)H); ^{13}C, δ 172.1 C(1), 132.8 C(2), 131.0 C(3), 140.9 C(4), 135.9 C(5), 128.1 C(6), 128.9 C(7), 126.2 C(8), 127.1 C(9). ESI-MS (−): *m/z* 429 (28.7%, Ag_2(Clpspa)), 448 (29.7%, Ag_2(Clpspa)Na), 642 (2.3%, Ag_2(HClpspa)(Clpspa)), 857 (7.5%, Ag_2(HClpspa)$_3$), 1071 (1.6%, Ag_4(HClpspa)(Clpspa)$_2$), 1282 (2.3%, Ag_4(Clpspa)$_4$), 1285 (1.0%, Ag_4(HClpspa)$_3$(Clpspa)).

*2.4.4.2. Na[Ag(-o-mpspa)]·H_2O (**17**).* [Ag(H-*o*-mpspa)] (0.15 g, 0,47 mmol), NaOH (0.019 g, 0.47 mmol), H_2O (15 cm^3). Yield 82%. Yellow solid, mp 155 °C (dec.). Anal. Found: C 33.1, H 2.6, S 8.6%. Calcd for $C_{10}H_{10}O_4SAgNa$: C 33.6, H 2.8, S 8.9%. IR (cm^{-1}): 1554 vs, $\nu_{as}(COO^-)$; 1364 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.72 (s, 1H, C(3)H), 8.54 (d, 1H, C(6)H), 6.89 (t, 1H, C(7)H), 7.16 (t, 1H, C(8)H), 6.91 (d, 1H, C(9)H), 3.75 (s, 3H, OCH_3); ^{13}C, δ 173.5 C(1), 126.5 C(2), 137.5 C(3), 125.7 C(4), 156.7 C(5), 110.2 C(6), 129.7 C(7), 119.3 C(8), 127.7 C(9), 55.1 C(OCH_3). ESI-MS (−): *m/z* 425 (4.2%, Ag_2(-*o*-mpspa)), 633 (1.4%, Ag_2(H-*o*-mpspa)(-*o*-mpspa)).

*2.4.4.3. Na[Ag(-o-hpspa)]·2H_2O (**18**).* [Ag(H-*o*-hpspa)] (0.11 g, 0.36 mmol), NaOH (0.014 g, 0.36 mmol), H_2O (11 cm^3). Yield 60%. Orange solid, mp 150 °C (dec.). Anal. Found: C 29.6, H 2.5, S 8.5%. Calcd for $C_9H_{10}O_5SAgNa$: C 29.9, H 2.8, S 8.9%. IR (cm^{-1}): 1549 vs, $\nu_{as}(COO^-)$; 1363 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.74 (s, 1H, C(3)H), - (s, 1H, C(5)OH), 6.76 (m, 2H, C(6)H and C(8)H), 6.98 (st, 1H, C(7)H), 8.49 (d, 1H, C(9)H); ^{13}C, δ 173.8 C(1), 124.2 C(2), 128.3 C(3), 132.0 C(4), 155.3 C(5), 114.7 C(6), 130.4 C(7), 118.2 C(8), 129.7 C(9). ESI-MS (−): *m/z* 409 (4.1%, Ag_2(-*o*-hpspa)), 434 (0.5%, Ag_2(-*o*-hpspa)Na), 607 (2.0%, Ag_2(H-*o*-hpspa)(-*o*-hpspa)), 803 (1.9%, Ag_2(H-*o*-hpspa)$_3$), 1208 (1.9%, Ag_4(-*o*-hpspa)$_4$), 1214 (1.9%, Ag_4(H-*o*-hpspa)$_3$(-*o*-hpspa)).

*2.4.4.4. Na[Ag(-p-hpspa)]·2H_2O (**19**).* [Ag(H-*p*-hpspa)] (0.06 g, 0.20 mmol), NaOH (0.008 g, 0.20 mmol), H_2O (6 cm^3). Yield 75%. Orange solid, mp 190 °C (dec.). Anal. Found: C 29.4, H 2.4, S 8.3%. Calcd for $C_9H_{10}O_5SAgNa$: C 29.9, H 2.8, S 8.9%. IR (cm^{-1}): 1547 vs, $\nu_{as}(COO^-)$; 1355 vs, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.46 (s, 1H, C(3)H), 7.87 (d, 2H, C(5)H, C(9)H), 6.71 (d, 2H, C(6)H, C(8)H), 9.50 (s, 1H, C(7)OH); ^{13}C, δ 172.1 C(1), 121.2 C(2), - C(3), - C(4), 131.5 C(5) and C(9), 114.6 C(6) and C(8), - C(7). ESI-MS (−): *m/z* 409 (9.1%, Ag_2(-*p*-hpspa)), 434 (4.3%, Ag_2(-*p*-hpspa)Na), 607 (1.6%, Ag_2(H-*p*-hpspa)(-*o*-hpspa)), 803 (1.5%, Ag_2(H-*p*-hpspa)$_3$), 1019 (0.9%, Ag_4(H-*p*-hpspa)(-*p*-hpspa)$_2$), 1208 (0.7%, Ag_4(-*p*-hpspa)$_4$), 1214 (0.9%, Ag_4(H-*p*-hpspa)$_3$(-*o*-hpspa)).

*2.4.4.5. Na[Ag(-diBr-o-hpspa)]·2H_2O (**20**).* [Ag(H-diBr-*o*-hpspa)] (0.08 g, 0.17 mmol), NaOH (0.007 g, 0.17 mmol), H_2O (8 cm^3). Yield 74%. Yellow solid, mp 160 °C (dec.). Anal. Found: C 20.6, H 1.3, S 5.9%. Calcd for $C_9H_8O_5SBr_2AgNa$: C 20.8, H 1.6, S 6.2%. IR (cm^{-1}): 1566 s, br, $\nu_{as}(COO^-)$; 1353 m, br, $\nu_{sym}(COO^-)$. NMR (DMSO-d_6): ^{1}H, δ 7.91 (s, 1H, C(3)H), - (br s, 1H, C(5)OH), 8.49 (d, 1H, C(7)H), 7.18 (d, 1H, C(9)H); ^{13}C, δ 173.8 C(1), 127.6 C(2), 134.2 C(3), 131.8 C(4), 155.6 C(5), 17.0 C(6), 132.6 C(7), 113.8 C(8), 133.3 C(9). ESI-MS (−): *m/z* 570 (8.9%, Ag_2(diBr-*o*-hpspa)), 590 (8.9%, Ag_2(diBr-*o*-hpspa)Na), 923 (1.0%, Ag_2(H-diBr-*o*-hpspa)(diBr-*o*-hpspa)), 1277 (1.0%, Ag_2(H-diBr-*o*-hpspa)$_3$), 1385 (0.9%, Ag_3(H-diBr-*o*-hpspa)$_2$(diBr-*o*-hpspa)).

3. Results and discussion

The stoichiometric reactions of $AgNO_3$ with H_2xspa gave compounds **1**–**3** in yields of 60–78%, but only poor yields of **4** and **5**, which were therefore obtained (in 60% and 72% yield, respectively) using Ag_2O (*Method B*). The remaining complexes (**6**–**20**) were prepared uneventfully as described in Section 2.4.

The four classes of compound prepared differ in solubility. The [HQ][Ag(L)] complexes (**11**–**15**) are soluble in ethanol, methanol, acetone and DMSO, the Na[Ag(L)]·$x$$H_2O$ complexes (**16**–**20**) in water and DMSO, the [Ag(HL)] complexes (**1**–**5**) only in DMSO, and the [Ag_2(L)] complexes (**6**–**10**) in none of the common solvents.

*3.1. Crystal and molecular structures of H_2Clpspa and [HQ][Ag(Clpspa)] (**11**)*

The single crystals obtained by slow evaporation of solvent from a solution of H_2Clpspa in $CDCl_3$ are composed of H_2Clpspa

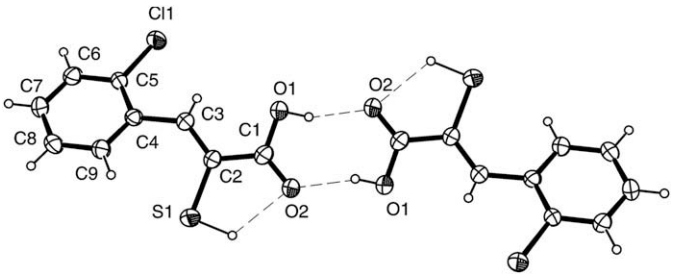

Fig. 1. Molecular structure of H_2Clpspa, with the numbering scheme used herein. Intra- and intermolecular hydrogen bonds are also shown.

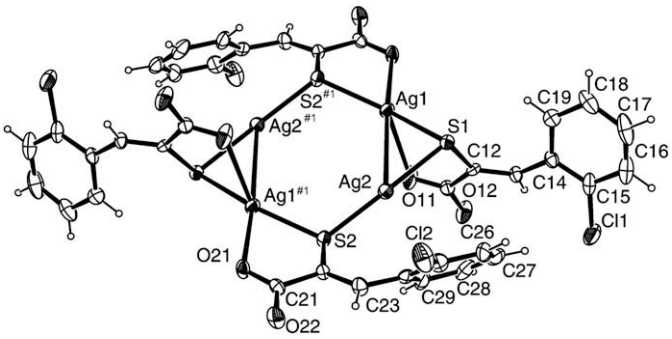

Fig. 2. Molecular structure of the $[Ag_4(Clpspa)_4]^{4-}$ anion, with the numbering scheme used herein. Probability ellipsoids are shown at the 30% level.

molecules linked dimerically by hydrogen bonds between their COOH groups as shown in Fig. 1; selected bond lengths and angles are listed in Table 2. The H_2Clpspa molecule has *Z* configuration about the C(2)–C(3) bond, and the phenyl ring makes an angle of 32.83° with the plane defined by the sulfanylpropenoato skeleton, C(3)C(2)S(1)C(1)O(2)O(1). The C(2)–S(1) bond length, 1.766(7) Å, is close to those found in thiols such as 2-sulfanylnicotinic acid [30] [1.704(3) Å] or the dimethylformamide adduct of 2,3-dimercaptosuccinic acid [45] [1.839(3) Å], and is also close to 1.774(4) and 1.767(4) Å found in the two slightly different molecules of $(Htspa)_2 \cdot Me_2CO$, an S–S bonded dimer we obtained [46] while trying to crystallize 3-(2-thienyl)sulfanylpropenoic acid (H_2tspa). The C(1)–O(1) and C(1)–O(2) bond lengths are both at the lower limits of the ranges 1.31–1.35 Å and 1.21–1.25 Å that are typical of the C–O and C=O bonds in an ordered carboxylic acid dimer [47]. As well as the dimerizing hydrogen bonds [O(1)–H(1)–$O(2)^{\#1}$: 1.06(9), 1.64(9), 2.646(7) Å, 157(8)°; #1 = $(-x, -y+1, -z)$], each molecule also has an intramolecular hydrogen bond between its SH and COOH groups [S(1)–H(1)–O(2): 1.27(8), 2.09(8) Å, 120(5)°].

The single crystals obtained by slow concentration of a solution of **11** in MeOH/DMSO are composed of {[HQ]$_4$[Ag_4(Clpspa)$_4$]} units. The structure of the $[Ag_4(Clpspa)_4]^{4-}$ anion in these units is shown in Fig. 2 together with the atom-numbering scheme, and selected bond lengths and angles are listed in Table 3. The central core of the anion is an Ag_4S_4 ring in which the S(1) and S(2) atoms lie, respectively, 0.2557(8) and 0.3225(9) Å from the Ag_4 plane. The Ag(1)–Ag(2) distance, 2.8986(9) Å, is just slightly longer than in metallic silver [2.889(6) Å], and is considerably shorter than twice the van der Waals radius of this metal (3.44 Å) [48], suggesting the existence of significant Ag–Ag interaction [14,28,38,49–53]. However, no interaction is suggested by the Ag(1)–$Ag(2)^{\#1}$ distance (#1 = $-x+1, -y, -z+1$), 4.1207(12) Å. The Ag–S bond lengths are all in the normal range [38], but both the Ag–S–Ag bridges are slightly asymmetric [Ag(1)–S(1)–Ag(2), 2.44415(19) and 2.4195(19) Å; Ag(1)$^{\#1}$–S(2)–Ag(2), 2.44137(19) and 2.3932(19) Å].

As in anion I of [HQ][Ag(pspa)] [28], the two Ag(1) atoms of the Ag_4S_4 ring are each chelated by the S and O(1) atoms of two sulfanylpropenoato ligands [S(1)–Ag(1)–$S(2)^{\#1}$, 150.80(6)°; Ag(1)–O(11), 2.633(5) Å; Ag(1)–$O(21)^{\#1}$, 2.506(5) Å], whereas the only strong metal–ligand coordinate bonds of Ag(2) are its Ag–S bonds, which are practically collinear [S(1)–Ag(2)–S(2), 175.96(6)°]. Thus if Ag–Ag bonds and other weak interactions are ignored, the coordination polyhedron of Ag(1) is a distorted tetrahedron, AgS_2O_2, whereas the environment of Ag(2) is essentially linear, of type AgS_2. However, apart from its interaction with Ag(1), Ag(2) also appears to have weak interactions with two of the carbons of a nearby phenyl ring [54,55], the Ag(2)–C(29) and Ag(2)–C(24) distances (respectively, 2.958(7) and 3.131(6) Å) both being shorter than the sum of the van der Waals radii (3.40) [48].

As well as anion I of [HQ][Ag(pspa)], the structure of $[Ag_4(Clpspa)_4]^{4-}$ recalls that of $[Ag_4\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_4]$ [56]. [HQ][Ag(Clpspa)] contains no anions that are structurally analogous to anion II of [HQ][Ag(pspa)], in which each Ag atom of the Ag_4S_4 ring is chelated by just a single $pspa^-$ ligand [28].

The HQ cations of [HQ][Ag(Clpspa)] interact with the $[Ag_4(Clpspa)_4]^{4-}$ anions through a complex set of hydrogen bonds involving all the carboxylate O atoms (Table 4). A view of the resulting structure is shown in Fig. 3.

3.2. IR spectra

The IR spectra of [Ag(HL)] complexes do not show the ν(SH) band that appears at around 2560 cm^{-1} in the spectra of the free ligands. Furthermore, the vibrations of the COOH group are only slightly shifted from their positions in the spectra of the free ligands [ν(C=O) = 1683, 1664, 1682, 1686 and 1682 cm^{-1} for H_2Clpspa, H_2-*o*-mpspa, H_2-*o*-hpspa, H_2-*p*-hpspa and H_2-diBr-*o*-hpspa, respectively]. Both features are compatible with [Ag(HL)] having a polymeric structure in which the monomers are linked by Ag–S bonds and the COOH groups are neither deprotonated nor coordinated. Similar structures have been hypothesized for [Ag(Hpspa)] [28] and [Ag(Hmba)] [23,24].

Table 2
Selected bond lengths (Å) and angles (°) in H_2Clpspa

Cl(1)–C(5)	1.737(7)	S(1)–C(2)	1.766(7)
O(1)–C(1)	1.312(9)	C(1)–O(2)	1.206(8)
C(1)–C(2)	1.467(10)	C(2)–C(3)	1.324(9)
C(3)–C(4)	1.461(10)	C(4)–C(9)	1.393(9)
C(4)–C(5)	1.405(9)	C(5)–C(6)	1.378(10)
C(6)–C(7)	1.362(11)	C(7)–C(8)	1.364(11)
C(8)–C(9)	1.366(9)		
O(2)–C(1)–O(1)	122.0(7)	O(2)–C(1)–C(2)	123.2(7)
O(1)–C(1)–C(2)	114.8(6)	C(3)–C(2)–C(1)	120.4(7)
C(3)–C(2)–S(1)	123.8(6)	C(1)–C(2)–S(1)	115.6(5)
C(2)–C(3)–C(4)	131.4(7)	C(9)–C(4)–C(5)	115.9(6)
C(9)–C(4)–C(3)	123.8(6)	C(5)–C(4)–C(3)	120.3(6)
C(6)–C(5)–C(4)	121.7(6)	C(6)–C(5)–Cl(1)	117.5(5)
C(4)–C(5)–Cl(1)	120.8(5)	C(7)–C(6)–C(5)	119.8(7)
C(8)–C(7)–C(6)	120.2(7)	C(7)–C(8)–C(9)	120.3(7)
C(8)–C(9)–C(4)	122.0(7)		

Table 3
Selected bond lengths (Å) and angles (°) in [HQ][Ag(Clpspa)] (**11**)

Ag(1)–S(1)	2.44415(19)	S(1)–Ag(1)–$S(2)^{\#1}$	150.80(6)
Ag(1)–$S(2)^{\#1}$	2.44137(19)	S(1)–Ag(1)–$O(21)^{\#1}$	75.05(12)
Ag(1)–O(11)	2.633(5)	S(1)–Ag(1)–$O(21)^{\#1}$	126.65(12)
Ag(1)–$O(21)^{\#1}$	2.506(5)	S(1)–Ag(2)–S(2)	175.96(6)
Ag(1)–Ag(2)	2.8986(9)	S(1)–Ag(1)–O(11)	73.42(12)
Ag(2)–S(1)	2.4195(19)	$S(2)^{\#1}$–Ag(1)–O(11)	125.28(12)
Ag(2)–S(2)	2.3932(19)	O(11)–Ag(1)–$O(21)^{\#1}$	102.25(17)

#1: $-x+1, -y, -z+1$.

Table 4
Hydrogen bonds in [HQ][Ag(Clpspa)] (**11**)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)–H(1A)···O(12)	0.90	1.84	2.732(7)	168.3
N(1)–H(1B)···O(21)$^{\#2}$	0.90	1.88	2.762(6)	165.3
N(1)–H(1B)···O(22)$^{\#2}$	0.90	2.63	3.361(7)	138.5
N(2)–H(2A)···O(11)	0.90	1.83	2.715(7)	166.7
N(2)–H(2B)···O(22)$^{\#2}$	0.90	1.84	2.729(7)	172.0

#1: $-x+1, -y, -z+1$; #2: $-x+3/2, y+1/2, -z+3/2$.

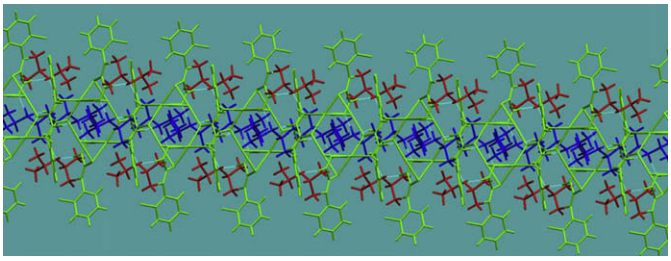

Fig. 3. A partial perspective view of the crystal packing in **11**, as seen along the *b* axis.

The spectra of the $[Ag_2(L)]$, [HQ][Ag(L)] and $Na[Ag(L)]\cdot xH_2O$ complexes lack both the ν(SH) band and the COOH bands, suggesting bideprotonation of the ligand. For example, the spectrum of [HQ][Ag(Clpspa)] (**11**) shows neither the ν(SH) band located at 2561 cm^{-1} in the spectrum of the free acid nor its COOH bands at 1683 cm^{-1} [ν(C=O)], 1437 cm^{-1} [δ(OH)] and 1259 cm^{-1} [ν(C–O)], which are replaced by bands typical of a carboxylato group at 1552 cm^{-1} [$\nu_{as}(COO^-)$] and 1348 cm^{-1} [$\nu_{sym}(COO^-)$]. That for compound **11** $\nu_{as}(COO^-)$ and $\nu_{sym}(COO^-)$ are separated by only 204 cm^{-1}, a smaller $\Delta\nu$ value than is usual for complexes in which a carboxylato group coordinates through just one of its O atoms [57,58], is attributed, as in the case of similar L^{2-} complexes [28,59], to the significant lengthening of the $C–O_{uncoordinated}$ bond by one or more N–H···O hydrogen bonds; and the fact that all the [HQ][Ag(L)] compounds have $\nu_{as}(COO^-)$ and $\nu_{sym}(COO^-)$ near their positions in the spectrum of **11** suggests that in all of them, as in **11**, the L^{2-} ligand is coordinated through its S atom and just one of its carboxylate O atoms, the other being hydrogen bonded to the HQ cations. Similarly, the positions of these bands in the spectra of the $Na[Ag(L)]\cdot H_2O$ and $Na[Ag(L)]\cdot 2H_2O$ complexes [$\nu_{as}(COO^-)$ between 1566 and 1548 cm^{-1}, $\nu_{sym}(COO^-)$ between 1365 and 1353 cm^{-1}] suggest that these compounds, too, share this kind of coordination mode, with the N–H···O bonds of [HQ][Ag(L)] replaced by hydrogen bonds with H_2O molecules. That the carboxylate bands of the $[Ag_2(L)]$ complexes also appear in these regions suggesting that in compounds **6**–**10** the carboxylato group acts as a bis-monodentate bridge between Ag atoms [38], creating a polymeric structure that would explain the poor solubility of these compounds.

3.3. Solution studies

The ^{1}H NMR spectra of the complexes of type [Ag(HL)] (**1**–**5**) retain the broad signal seen at about 13 ppm in the spectra of the ligands, in keeping with the non-deprotonation of the COOH group. In the ^{13}C NMR spectra of these complexes the C(3) signal lies upfield of its positions in those of the free ligands (135.1, 139.5, 130.3 and 132.7 ppm in H_2Clpspa, H_2-*o*-mpspa, H_2-*o*-hpspa and H_2-*p*-hpspa, respectively), suggesting that, as in other complexes with these ligands [38,46], the S-coordination found in the solid state persists in solution.

In the ^{1}H NMR spectra of the [HQ][Ag(L)] and $Na[Ag(L)]\cdot xH_2O$ compounds, the upfield shift of the C(3)H signal from its positions in the free ligand spectra suggests the persistence of the S–Ag bond in solution, while the disappearance of the broad free ligand signal

Table 5
Antimicrobial activities (MICs) of the complexes prepared in this work and other compounds containing Ag–S bonds

Compound	*E. coli*	*S. aureus*	*B. subtilis*	*P. aeruginosa*	Resistant *P. aeruginosa*	*C. albicans*
[HQ][Ag(pspa)][a]	200	100	50	25	25	50
[HQ][Ag(fspa)][a]	200	50	50	25	25	50
[HQ][Ag(tspa)][a]	>200	200	100	100	50	50
[HQ][Ag(-*o*-pyspa)][a]	200	200	100	100	100	100
[HQ][Ag(cpa)][a]	>200	>200	100	200	100	200
[HQ][Ag(Clpspa)](**11**)[b]	200	50	50	25	25	100
[HQ][Ag(-*o*-mpspa)](**12**)[b]	100	50	50	12.5	25	25
[HQ][Ag(-*o*-hpspa)](**13**)[b]	200	100	25	25	>200	25
[HQ][Ag(-*p*-hpspa)](**14**)[b]	200	100	25	25	>200	25
[HQ][Ag(-diBr-*o*-hpspa)](**15**)[b]	200	100	25	50	25	100
$Na[Ag(pspa)]\cdot H_2O$[a]	>200	25	25	50	25	50
$Na[Ag(fspa)]\cdot H_2O$[a]	100	25	12.5	25	6.25	50
$Na[Ag(tspa)]\cdot H_2O$[a]	100	25	25	50	25	100
$Na[Ag(cpa)]\cdot H_2O$[a]	>200	50	>200	>200	>200	50
$Na[Ag(Clpspa)]\cdot H_2O$(**16**)[b]	>200	12.5	12.5	50	12.5	>200
$Na[Ag(-o-mpspa)]\cdot H_2O$(**17**)[b]	>200	12.5	12.5	50	12.5	50
$Na[Ag(-o-hpspa)]\cdot 2H_2O$(**18**)[b]	200	200	100	200	200	>200
$Na[Ag(-p-hpspa)]\cdot 2H_2O$(**19**)[b]	100	>200	6.25	50	25	50
$Na[Ag(-diBr-o-hpspa)]\cdot 2H_2O$(**20**)[b]	>200	50	200	>200	>200	>200
Ag–S						
$\{Na[Ag(Htma)]\cdot 0.5H_2O\}_n$[c]	31.3	>2000	>2000	31.3		>2000
$\{Na[Ag(mba)]\cdot H_2O\}_n$[d]	<2	32	<2	16		1000
$[Ag(Hmba)]_n$[d]	<2	16	<2	16		1000
Ag–S Ag–N						
$[Ag(Hmna)]_6$[e]	25	25	25	12.5		50
$\{Na[Ag(mna)]\}_n$[e]	15.7	>1000	>1000	31.3		>1000

MIC = Minimum inhibitory concentration (μg/mL).
[a] Ref. 28.
[b] This work.
[c] Ref. 22.
[d] Refs. 23,24.
[e] Ref. 25.

near 13 ppm indicates the deprotonation of the COOH group. In the ^{13}C NMR spectra, the persistence of S-coordination is confirmed by the lowfield shifts of the C(3) signal, and the persistence of coordination to COO^- is suggested by the C(1) signals being practically in the same position as in compounds known to have a coordinated carboxylato group [59,60]. The existence of polynuclear anions in solutions of these complexes was studied by ESI-MS, a soft ionization technique that has proved useful for detecting polynuclearity in the cases of other silver(I) compounds [28]. The ESI-MS spectra of several complexes show one or more peaks corresponding to counterparts of the tetranuclear ion $[Ag_4(Clpspa)_4]^{4-}$ observed in the X-ray study of [HQ][Clpspa], together with peaks for ions of lesser nuclearity; in particular, a dinuclear fragment is present in all these spectra.

Studies of the $[Ag_2(L)]$ compounds in solution were prevented by their insolubility.

3.4. Antimicrobial activity

Neither the ligands nor complexes of types [Ag(HL)] and $[Ag_2(L)]$ (**1**–**10**) exhibited any activity of note, and the same absence of activity has been reported for diisopropylammonium chloride [59] and for the complexes of these types described in Ref. 28. The inactivity of **1**–**10** and related complexes [28] is attributable to their poor solubility, but nevertheless contrasts with the behaviour of $[Ag(Hmba)]_n$, a water-soluble oligomer with Ag–S bonds and uncoordinated –COOH groups that appears to be structurally similar and shows significant activity against the bacteria employed in the present study [23,24].

Table 5 lists the minimum inhibitory concentrations of the new [HQ][Ag(L)] and $Na[Ag(L)]\cdot xH_2O$ compounds for the test organisms, and corresponding data for some related compounds are listed in Tables 5 and 6. In general, the activity spectra of the new compounds are similar to those of their most closely related analogues [28]: some of the $Na[Ag(L)]\cdot xH_2O$ complexes are somewhat more active than the corresponding diisopropylammonium derivatives, and no compound has more than very slight activity against *E. coli*. In comparison with $Na[Ag(pspa)]\cdot H_2O$, $Na[Ag(Clpspa)]\cdot H_2O$ was more active against *S. aureus*, *B. subtilis* and resistant *P. aeruginosa*, and less active against *C. albicans*. Overall, however, the best MIC values are those of the *o*-mpspa derivative (**17**), although the MIC of $Na[Ag(-p\text{-}hpspa)]\cdot 2H_2O$ against *B. subtilis*, 6.25 μg/mL, may also be noted.

Both the new compounds and those described in Ref. 28 are more active than $\{Na[Ag(mba)]\cdot H_2O\}_n$ [23,24] against *C. albicans*, but less active against the bacteria used in this study. Some show activities that are similar to those of $[Ag(Hmna)]_6$ [25] and are greater than those of $\{Na[Ag(Htma)]\cdot 0.5H_2O\}_n$ (H_3tma = thiomalic acid) [22] and $\{Na[Ag(mna)]\}_n$ [25] against all the test organisms except *E. coli*.

Due largely to their low activity against *E. coli*, the antimicrobial spectra of compounds with Ag–S bonds have generally been narrower than those of Ag–N- and Ag–O-bonded compounds. However, the activity of **17** against the test organisms other than

Table 6
Antimicrobial activities (MICs) of silver(I) complexes containing Ag–N and Ag–O bonds

Compound	*E. coli*	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*C. albicans*
Ag–N					
[Ag(imd)][a]	6.3	50	50	12.5	50
$[Ag(Himd)_2]NO_3$[a]	7.9	15.7	15.7	7.9	15.7
$[Ag(1,2,3\text{-}triaz)]_n$[b]	250	500	>1000	500	1000
$[Ag(1,2,4\text{-}triaz)]_n$[b]	4.0	7.9	125	7.9	15.7
$\{[Ag(Hhis)]_2\}_n$[c]	15.7	62.5	62.5	15.7	15.7
$\{[Ag(Hhis)]\}_n$[c]	125	250	250	250	125
$[Ag(tetz)]_n$[d]	4	15.7	15.7	15.7	31.3
Ag–O					
$\{[Ag(\text{L-}Hasp)]\}_n$[e]	125	125	125	125	31.3
$\{[Ag(\text{D-}Hasp)]\}_n$[e]	62.5	125	125	62.5	31.3
$\{[Ag_2(\text{D-}Hasp)(\text{L-}Hasp)]\cdot 1.5H_2O\}_n$[e]	125	250	250	125	62.5
$\{[Ag(S\text{-}othf)]_2\}_n$[f]	15.7	31.3	31.3	15.7	7.9
$\{[Ag(R\text{-}othf)]_2\}_n$[f]	7.9	15.7	62.5	15.7	15.7
$[Ag_2(S\text{-}othf)(R\text{-}othf)]_n$[f]	7.9	62.5	62.5	31.3	15.7
$\{[Ag(S\text{-}Hpyrrld)]_2\}_n$[g]	7.9	31.3	15.7	7.9	7.9
$\{[Ag(R\text{-}Hpyrrld)]_2\}_n$[g]	15.7	31.3	31.3	15.7	7.9
$[Ag_2(S\text{-}Hpyrrld)(R\text{-}Hpyrrld)]_n$[g]	15.7	31.3	31.3	15.7	7.9
$[Ag(hino)]_2$[h]	125	125	500	250	31.3
$\{[Ag_2\text{-}(R\text{-}ca)]_2\}_n$[i]	62.5	125	125	62.5	62.5
$\{[Ag_2\text{-}(S\text{-}ca)]_2\}_n$[i]	31.3	250	250	31.3	62.5
$\{[Ag_2(R\text{-}ca)\text{-}(S\text{-}ca)]\}_n$[i]	31.3	125	125	62.5	62.5
$\{[Ag_2(R\text{-}ca)_2\text{-}(R\text{-}Hca)_2]\}_n$[i]	125	125	250	250	62.5
$\{[Ag_2(S\text{-}ca)_2\text{-}(S\text{-}Hca)_2]\}_n$[i]	31.3	125	125	31.3	31.3
Achiral $\{[Ag_2(ca)_2\text{-}(Hca)_2]\}_n$[i]	62.5	62.5	250	62.5	15.7
$[Ag(LV)_2]$[j]	62.5	62.5	<31.2	<31.2	31.2

MIC = Minimum inhibitory concentration (μg/mL). *Nomenclature*: Htriaz = triazole; H_2his = L-histidine; H_2asp = aspartic acid; Hhino = 4-isopropyltropolone; *R*- and *S*-Hca: (1*R*,4*S*)- and (1*S*, 4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylic acid, respectively; LV = 2-[4,6-di(*tert*-butyl)-2,3-dihydroxyphenylsulfanyl]acetic acid. For others, see text.

[a] Ref. 13.
[b] Ref. 11.
[c] Ref. 14.
[d] Ref. 12.
[e] Ref. 18.
[f] Ref. 16.
[g] Ref. 17.
[h] Ref. 19.
[i] Ref. 15.
[j] Ref. 20.

E. coli is similar to that of active Ag–N compounds such as $[Ag(tetz)]_n$ (Htetz = tetrazole) [12], $[Ag(imd)]_n$ (Himd = imidazole) [13], $[Ag(Himd)_2]NO_3$ [13], [Ag(1,2,4-triaz)] (Htriaz = triazole) [11] and $\{[Ag(Hhis)]_2\}_n$ (H_2his = histidine) [14], and to that of Ag–O compounds such as $\{[Ag(S\text{-othf})]_2\}_n$ (Hothf = 5-oxo-2-tetrahydrofurancarboxylate) [16], $\{[Ag(R\text{-othf})]_2\}_n$ [16], $[Ag_2(S\text{-othf})(R\text{-othf})]_n$ [16], $\{[Ag(S\text{-Hpyrrld})]_2\}_n$ (H_2pyrrld = (S)-(−)-2-pyrrolidone-5-carboxylic acid) [17], $\{[Ag(R\text{-Hpyrrld})]_2\}_n$ [17], and $[Ag_2(S\text{-Hpyrrld})(R\text{-Hpyrrld})]_n$ [17].

Other Ag–O- or Ag–N-bonded silver(I) complexes that have been tested against bacteria and yeasts include derivatives of quinoxaline, 2,5-dimethylpyrazine and 3-aminopyridine, in all of which the metal atom is also coordinated to one or more nitrate anions [9]. These compounds are more active than **17** against *E. coli* and *P. aeruginosa*, and all except the 3-aminopyridine derivative are also more active against *C. albicans*. Good activity against this yeast is also shown by $[Ag_2(NH_3)_2(Hsal)_2]$ (H_2sal = salicylic acid) [61] and Ag(I) imidazole and bis-imidazole derivatives [62,63], some of which are also more active than **17** against *E. coli*.

4. Conclusions

The reactions of Ag(I) with 3-(substituted phenyl)-2-sulfanylpropenoic acids H_2L allow the preparation of compounds of types [Ag(HL)], $[Ag_2(L)]$, [HQ][Ag(L)] and $Na[Ag(L)]\cdot H_2O$ (HQ = diisopropylammonium). In H_2Clpspa crystals, the molecules are non-planar, and the SH and COOH groups are involved in intra- and intermolecular hydrogen bonds. Both these groups are deprotonated and coordinated to the silver atom in the $[Ag(Clpspa)]_4^{4-}$ anions present in crystals of [HQ][Ag(Clpspa)]. Solutions of [HQ][Ag(Clpspa)] in methanol contain both these tetranuclear and other multinuclear species.

The complexes of types [HQ][Ag(L)] and $Na[Ag(L)]\cdot xH_2O$, especially the latter, show activity against certain Gram-positive and Gram-negative bacteria, and also against the yeast *C. albicans*; this activity is similar to that shown by other compounds with Ag–N and/or Ag–O bonds except in the case of *E. coli*. In comparison with the unsubstituted pspa complexes, the introduction of ring substituents does not significantly change the activity of the [HQ][Ag(L)] complexes. For the $Na[Ag(L)].xH_2O$ derivatives the introduction of the –Cl or $–OCH_3$ substituents in the *ortho*-position slightly increases the activity. Further studies with a wider spectrum of electron-withdrawing or electron-donating substituents are necessary to provide a basis for the structure optimization of this class of silver complexes in order to search for more active compounds.

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References

[1] J.L. Clement, P.S. Jarrett, Metal-Based drugs 1 (1994) 467–486.
[2] S. Silver, FEMS Microbiol. Rev. 27 (2003) 341–353.
[3] I. Chopra, J. Antimicrob. Chemother. 59 (2007) 587–590.
[4] K. Nomiya, R. Noguchi, T. Shigeta, Y. Kondoh, K. Tsuda, K. Ohsawa, N. Chikaraishi Kasuga, M. Oda, Bull. Chem. Soc. Jpn. 73 (2000) 1143–1152.
[5] A.D. Russell, W.B. Hugo, Prog. Med. Chem. 31 (1994) 351–370.
[6] S.Y. Liau, D.C. Read, W.J. Pugh, J.R. Furr, A.D. Russell, Lett. Appl. Microbiol. 25 (1997) 279–283.
[7] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, J.O. Kim, J. Biomed. Mater. Res. 52 (2000) 662–668.
[8] S. Silver, A. Gupta, K. Matsui, J.F. Lo, Metal-Based Drugs 6 (1999) 315–320.
[9] M.A.M. Abu-Youssef, V. Langer, L. Öhrström, Dalton Trans. (2006) 2542–2550.
[10] V. Sambhy, M.M. MacBride, B.R. Peterson, A. Son, J. Am. Chem. Soc. 128 (2006) 9798–9808.
[11] K. Nomiya, K. Tsuda, N.C. Kasuga, J. Chem Soc., Dalton Trans. (1998) 1653–1659.
[12] K. Nomiya, R. Noguchi, M. Oda, Inorg. Chim. Acta 298 (2000) 24–32.
[13] K. Nomiya, K. Tsuda, T. Sudor, M. Oda, J. Inorg. Biochem. 68 (1997) 39–44.
[14] K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama, M. Oda, Inorg. Chem. 39 (2000) 3301–3311.
[15] N. Chikaraishi Kasuga, A. Sugie, K. Nomiya, Dalton Trans. (2004) 3732–3740.
[16] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 1343–1348.
[17] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 4369–4373.
[18] K. Nomiya, H. Yokoyama, J. Chem. Soc., Dalton Trans. (2002) 2483–2490.
[19] K. Nomiya, A. Yoshizawa, K. Tsukagoshi, N. Chikaraishi Kasuga, S. Hirakawa, J. Watanabe, J. Inorg. Biochem. 98 (2004) 46–60.
[20] N.V. Loginova, A.A. Chernyavskaya, G.I. Polozov, T.V. Koval'chuck, E.V. Bondarenko, N.P. Osipovich, A.A. Sheryakov, O.I. Shadyro, Polyhedron 24 (2005) 611–618.
[21] B.S. Creaven, D.A. Egan, K. Kavanagh, M. McCann, M. Mahon, A. Noble, B. Thati, M. Walsh, Polyhedron 24 (2005) 949–957.
[22] K. Nomiya, K. Onoue, Y. Kondoh, N.C. Kasuga, H. Nagano, M. Oda, S. Sakuma, Polyhedron 14 (1995) 1359–1367;
K. Nomiya, K. Onoue, Y. Kondoh, N.C. Kasuga, H. Nagano, M. Oda, S. Sakuma, Polyhedron 15 (1996) 2303.
[23] K. Nomiya, Y. Kondoh, K. Onoue, N.C. Kasuga, H. Nagano, M. Oda, T. Sudoh, S. Sakuma, J. Inorg. Biochem. 58 (1995) 255–267.
[24] M. Oda, H. Itoh, T. Sudo, S. Sakuma, K. Nomiya, Y. Suzuki, Y. Jyonoshita, A. Kikuchi, Y. Takabatake, PTC. WO95/12602, 1995.
[25] K. Nomiya, S. Takahashi, R. Noguchi, J. Chem. Soc., Dalton Trans. (2000) 2091–2097.
[26] H.V. Rasika Dias, K.H. Batdorf, M. Fianchini, H.V.K. Diyabalanage, S. Carnahan, R. Mulcahy, A. Rabiee, K. Nelson, L.G. van Waasbergen, J. Inorg. Biochem. 100 (2006) 158–160.
[27] M.C. Gimeno, A. Laguna, Comprehensive Coordination Chemistry II, vol. 6, Elsevier, Oxford, 2004, pp. 911–1145.
[28] E. Barreiro, J.S. Casas, M.D. Couce, A. Sánchez, R. Seoane, J. Sordo, J.M. Varela, E.M. Vázquez-López, Dalton Trans. (2007) 3074–3085.
[29] K. Nomiya, R. Noguchi, C. Kato, Chem. Lett. (2000) 162–163.
[30] P.C. Zachariadis, S.K. Hadjikakou, N. Hadjiliadis, A. Michaelides, S. Skoulika, Y. Ming, Y. Xiaolin, Inorg. Chim. Acta 343 (2003) 361–365.
[31] I. Tsyba, B.B.-K. Mui, R. Bau, R. Noguchi, K. Nomiya, Inorg. Chem. 42 (2003) 8028–8032.
[32] Q. Li, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Chem.—Eur. J. 10 (2004) 1456–1462.
[33] Q. Li, M.F.C. Guedes da Silva, Z. Jinghua, A.J.L. Pombeiro, J. Organomet. Chem. 689 (2004) 4584–4591.
[34] B.S. Creaven, D.A. Egan, K. Kavanagh, M. McCann, A. Noble, B. Thati, M. Walsh, Inorg. Chim. Acta 359 (2006) 3976–3984.
[35] B. Thati, A. Noble, B.S. Creaven, M. Walsh, M. McCann, K. Kavanagh, M. Devereux, D.A. Egan, Cancer Lett. 248 (2007) 321–331.
[36] C. Gränacher, Helv. Chim. Acta 5 (1922) 610–624.
[37] E. Campaigne, R.E. Cline, J. Org. Chem. 21 (1956) 32–38.
[38] E. Barreiro, J.S. Casas, M.D. Couce, A. Sánchez, J. Sordo, J.M. Varela, E.M. Vázquez-López, Dalton Trans. (2005) 1707–1715.
[39] P. Álvarez-Boo, J.S. Casas, M.D. Couce, V. Fernádez-Moreira, E. Freijanes, E. García-Martínez, J. Sordo, E.M. Vázquez-López, Eur. J. Inorg. Chem. (2005) 4425–4429.
[40] Bruker Analytical Instrumentation, SAINT: SAX Area Detector Integration, 1996.
[41] G.M. Sheldrick, Sadabs, Version 2.03, University of Göttingen, Germany, 2002.
[42] G.M. Sheldrick, SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[43] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. MacCae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. B58 (2002) 389–397.
[44] E.W. Koneman, S.D. Allen, V.R. Dowell Jr., H.M. Sommers, Color Atlas and Textbook of Diagnostic Microbiology, J.B. Lippincott Co., USA, 1979, p. 321.
[45] G.J. Pyrka, N. Scott, Q. Fernando, Acta Crystallogr. C48 (1992) 2007–2009.
[46] E. Barreiro, J.S. Casas, M.D. Couce, A. Sánchez, J. Sordo, J.M. Varela, E.M. Vázquez-López, Dalton Trans. (2003) 4754–4761.
[47] B.M. Kariuki, C.L. Bauer, K.D.M. Harris, S.J. Tat, Angew. Chem., Int. Ed. 39 (2000) 4485–4488 and references therein.
[48] A. Bondi, J. Phys. Chem. 68 (1964) 441–551.
[49] M.J. Calhorda, P.J. Costa, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M. Naranjo, S. Quintas, Y.J. Shi, M.D. Villacampa, Dalton Trans. (2006) 4104–4113.
[50] M.R. Bermejo, A.M. Gonzalez-Noya, R.M. Pedrido, M.J. Romero, M. Vazquez, Angew. Chem., Int. Ed. 44 (2005) 4182–4187.
[51] Q.M. Wang, T.C.W. Mak, J. Am. Chem. Soc. 123 (2001) 7594–7600.
[52] L.S. Ahmed, J.R. Dilworth, J.R. Miller, N. Wheatley, Inorg. Chim. Acta 278 (1998) 229–231.
[53] W. Wojnowski, M. Wojnowski, K. Peters, E.M. Peters, H.G. von Schnering, Z. Anorg. Allg. Chem. 530 (1985) 79–88.
[54] I.F. Taylor Jr., E.A. Hall, E.L. Amma, J. Am. Chem. Soc. (1969) 5745–5749.
[55] V. Wing-Wah Yam, W.K.M. Fung, K.K. Cheung, Organometallics 16 (1997) 2032–2037.

[56] P. Perez-Lourido, J.A. Garcia-Vazquez, J. Romero, A. Sousa, E. Block, K.P. Maressa, J. Zubieta, Inorg. Chem. 38 (1999) 538–544.
[57] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed. John Wiley, New York, 1997, (Part B), p. 60.
[58] P. Alvarez Boo, J.S. Casas, M.D. Couce, R. Farto, J. Fernandez-Moreira, E. Freijanes, J. Sordo, E. Vazquez-Lopez, J. Organomet. Chem. 691 (2006) 45–52.
[59] J.S. Casas, A. Castiñeiras, M.D. Couce, M.L. Jorge, U. Russo, A. Sánchez, R. Seoane, J. Sordo, J.M. Varela, Appl. Organomet. Chem. 14 (2000) 421–431.
[60] J. Holecek, A. Lycka, M. Nadvornik, K. Handlir, Collect. Czech. Chem. Commun. 56 (1991) 1908–1915.
[61] B. Coyle, M. McCann, K. Kavanagh, M. Devereux, V. McKee, N. Kayal, D. Egan, C. Deegan, G.J. Finn, J. Inorg. Biochem. 98 (2004) 1361–1366.
[62] S. Abuskhuna, J. Briody, M. McCann, M. Devereux, K. Kavanagh, J. Barreira Fontecha, V. McKee, Polyhedron 23 (2004) 1249–1255.
[63] R. Rowan, T. Tallon, A.M. Sheahan, R. Curran, M. McCann, K. Kavanagh, M. Devereux, V. McKee, Polyhedron 25 (2006) 1771–1778.