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Synthesis and characterization of novel simultaneous C and O-coordinated and nitrate-bridged complexes of silver(I) with carbonyl-stabilized sulfonium ylides and their antibacterial activities†

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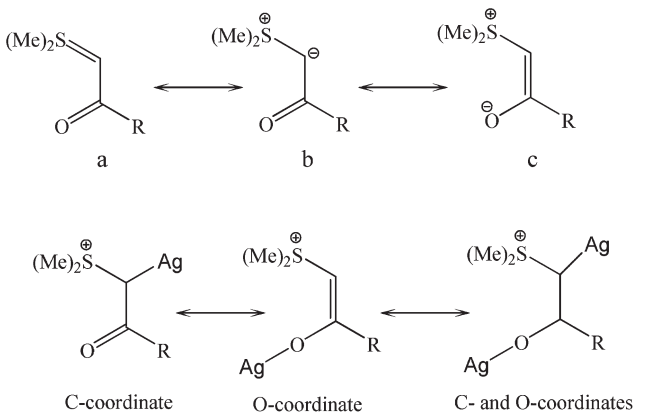
Reaction of sulfonium ylides $(Me)_2SCHC(O)C_6H_4R$ (R = H; *m*-NO_2; *p*-NO_2; *p*-OMe; *p*-Me and *p*-Br) with $AgNO_3$ in dichloromethane leads to various compounds. Single crystal X-ray diffraction analysis reveals that the adducts take 3 forms: (i) two-dimensional polymer, $[AgNO_3(Me_2SCHC(O)C_6H_5)]_n$ (**1**), with nitrate bridges in which each nitrate coordinates to three silver atoms through two oxygen atoms and two $Me_2SCHC(O)C_6H_5$ ligands coordinate to silver centers through carbon atoms; (ii) cationic binuclear, $[Ag(Me_2SCHC(O)C_6H_4\text{-}m\text{-}NO_2)_2]_2(NO_3)_2\cdot 2H_2O$ (**2**), in which $Me_2SCHC(O)C_6H_4$-*m*-NO_2 ligands simultaneously coordinate through both carbon and oxygen atoms with nitrate as a counter ion, and (iii) cationic mononuclear and anionic binuclear, $[Ag(Me_2SCHC(O)C_6H_4\text{-}p\text{-}NO_2)_2]_2[\{AgNO_3(\mu\text{-}NO_3)(Me_2SCHC(O)C_6H_4\text{-}p\text{-}NO_2)\}_2]\cdot 2CH_3OH$ (**3**), in which nitrate groups act as bridging as well as terminal ligands, and $Me_2SCHC(O)C_6H_4$-*p*-NO_2 ligands display C-coordination. Characterization of the obtained compounds was also performed by infrared, ^1H- and ^{13}C-NMR spectroscopy and analytical data indicated a 1 : 2 stoichiometry between the silver(I) nitrate and ylide *p*-OMe (**4**) and 1 : 1 for ylides *p*-Me (**5**) and *p*-Br (**6**). In addition, the antibacterial effects of DMSO-solutions of complexes **1–6** were evaluated by the agar disc diffusion method against three Gram positive and three Gram negative bacteria. All complexes displayed antibacterial activity against these bacteria, with high levels of inhibitory potency exhibited against the Gram negative species.

Introduction

In contrast to the numerous reported examples of silver(I) complexes of phosphonium ylide, sulfonium analogs have not been observed so far. Only one type of silver(I) complex for α-keto stabilized phosphorus ylides is known, $[Ag(Y)_2]X$, with Y = $Ph_3PCHCOR$ (R = aryl or alkyl) and X = NO_3, ClO_4 or OTF.[1–4] The potential richness in terms of coordinative versatility of sulfur–ylides (Scheme 1), and the use of these compounds in organic[5–8] and organometallic reactions, led us to the present study. Herein we report the synthesis of various stable silver(I) complexes, which are the first with carbonyl-stabilized sulfur ylides and the single crystal X-ray structures of examples of three structural types. The development of materials with the ability to inhibit bacterial growth have been



Scheme 1 The canonical forms of $(Me)_2SCHC(O)C_6H_4R$ (R = H; *m*-NO_2; *p*-NO_2; *p*-OMe; *p*-Me and *p*-Br) and their various coordination modes to a silver(I) center.

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of great interest in recent years due to their potential use in everyday products like paints, kitchenware, school and hospital utensils, *etc.* Nowadays, microorganisms resistant to multiple antimicrobial agents are serious problems worldwide in the fight against infectious diseases, increasing morbidity and mortality with an overall increase in health care costs.[9–11] For these reasons, there is an urgent need to develop novel antimicrobial agents with difficult mechanisms of action aimed at a better understanding of the antimicrobial resistance. It is well known that silver ions and silver-based compounds are highly toxic to microorganisms.[12,13] Various forms of silver and its compounds have been investigated in the past few decades due to the antimicrobial activity of silver ions, and there is an increased interest in the potential use of silver(I) as a therapeutic agent for different antimicrobial applications.[14–20] It is well established that only silver in its ionic or complex forms has antimicrobial activity, while elemental silver, even in the so-called "nanocrystalline" state is not.[21] Silver containing compounds are attractive because of the fact that in the range of the applicable concentrations, silver ions have limited toxicity because there is some research that has shown that although not a large amount, the ions do have some toxicity.[22–24] In the present work, a series of silver(I) complexes were prepared and characterized and their antibacterial activities were evaluated (Scheme 2).

Results and discussion

Spectroscopy

In the infrared spectra the carbonyl stretch that is sensitive to complexation, occurs at about 1551–1580 cm^{-1} for the parent ylides, as in the case of other resonance stabilized ylides.[25] Coordination of the ylide through carbon causes an increase in ν(CO), while for O-coordination a decrease of ν(CO) is expected. The infrared absorption bands observed for all our complexes at about 1661–1686 cm^{-1} suggest coordination of the ylide through the carbon atom. The infrared data were inconclusive in this project because of overlap of ν(NO) and $\nu(NO_2)$ bonds of the NO_3^- group with the ylide bonds.[1]

Although two diastereoisomers (RR (**1**) and SS/RS (**2** and **3**)) are possible for each complex (because the methine carbons are chiral), ^{1}H NMR spectroscopy does not distinguish between them at room temperature, even at 400 MHz and the methine resonances are intermediate between these diastereoisomers.[1–3] The ^{1}H NMR signals for the SCH group of complexes **1–6** are shifted downfield compared to those of the free ylides, as a consequence of the inductive effect of the metal center. The appearance of single signals for the SCH group in ^{1}H NMR at ambient temperature indicates the presence of only one geometrical isomer for all complexes as expected for C-coordination. It must be noted that O-coordination of the ylide leads to the formation of *cis* and *trans* isomers giving rise to two different signals in ^{1}H NMR spectrum.[26] The ^{13}C chemical shifts of the carbonyl carbon atoms in complexes **1–6** are around 187 ppm, relative to ~182 ppm noted for the same carbon in the parent ylides, indicating decreased shielding of this carbon atom in silver complexes. Interestingly, although ylide $Me_2SCHC(O)C_6H_4$-*m*-NO_2 coordinates to complex **2** through carbon and oxygen simultaneously, but the infrared and NMR spectra show only C-coordination. It should arise from an extremely poor band between oxygen and silver centers that can also be confirmed with the related bond length in the X-ray crystal structure. No coupling to Ag (^{109}Ag, 48.18% abundance, I = 1/2) was observed at room temperature in ^{1}H and ^{13}C NMR spectra. It is possible that a fast equilibrium between complexes and the free ylides is responsible for the failure to observe either NMR couplings or the presence of two diastereoisomers.[1]

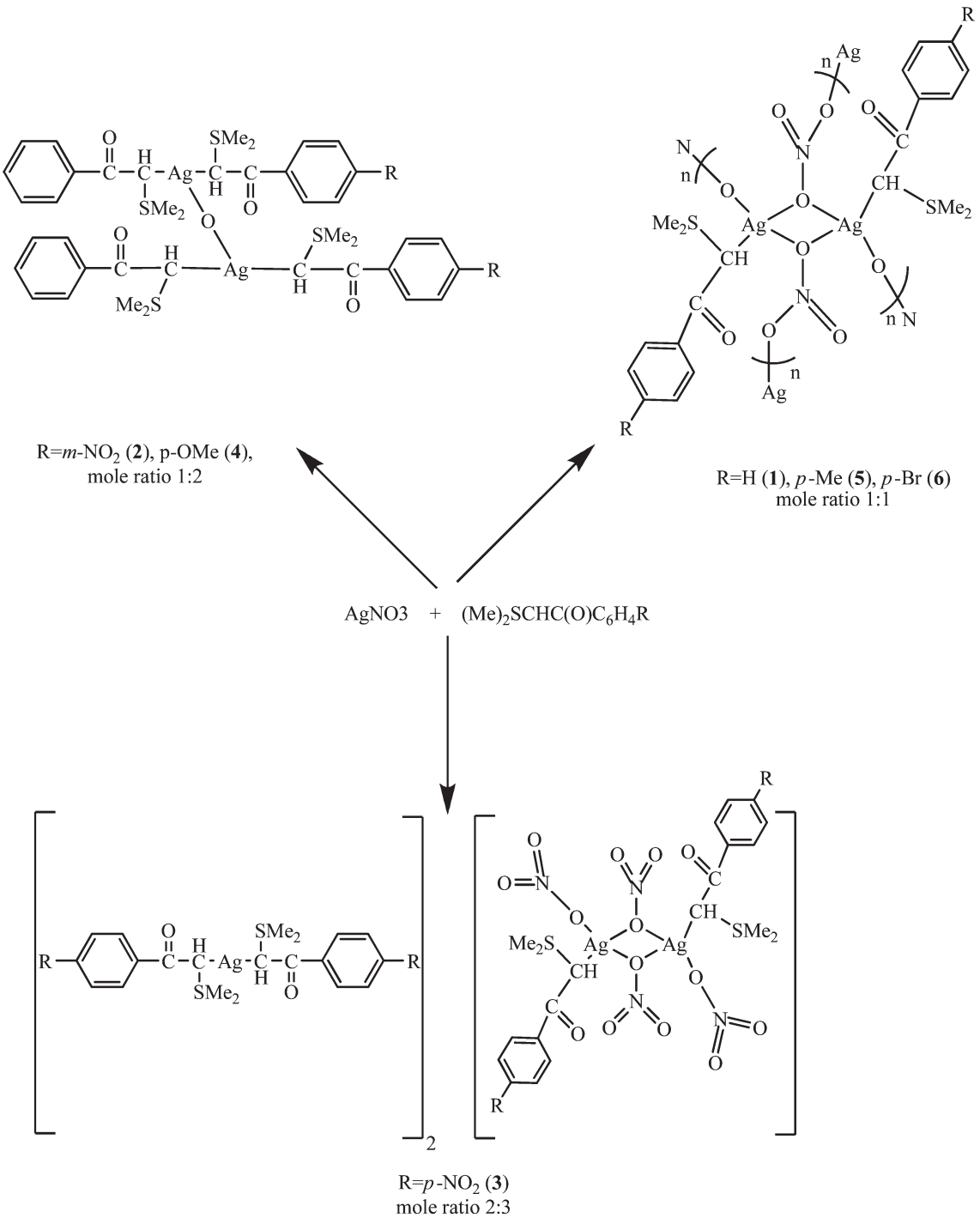
X-ray crystallography

The molecular structures of **1**, **2** and **3** were determined through single crystal X-ray diffraction methods. The molecular drawing of complexes **1**, **2** and **3** are shown in Fig. 1–3. Crystallographic data and parameters concerning data collection and structure solution and refinement are summarized in Table 1 and selected bond distances and angles are presented in Tables 2 and 3, respectively. Crystallographic data for all of the structures in this paper can be found in the ESI.†

Compound **1** is a polymer and one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure (Fig. 1a and 1b). The silver(I) center in the monomer is four-coordinate with sp^3 hybridization. This environment involves one nitrate Ag–O4 bond (connects the monomers together and comprises the polymer), one Ag–C bond and two asymmetric bridging Ag–O bonds of two different nitrates. The angles subtended by the ligands at the silver(I) center vary from 83.46(7)° to 158.88(9)° indicating a very distorted tetrahedral coordination geometry. The unsymmetrical nitrate coordination is reflected in its geometry, with N1–O4 longer than N1–O2 and O4–N1–O2 reduced to 118.8(2)°. Vicente *et al.*[1] reported a quasi-linear structure for the phosphorus analog with the same substituent in which nitrate ions are loosely associated with the metal center. The Ag–Cα (ylide), C═O and CO–Cα bond lengths (Table 2) are very close to the sulfonium analog, complex **1**, within experimental error. This similitude is worthy of note, taken into account that sulfur ylides are more basic than phosphorus ylides, provided that the two have the same substituents.[27]

The configuration at the chiral carbon atoms in compound **2** are RS for Ag1 and SS for Ag2. The silver atoms display two different coordination geometries one of which is two-coordinate and quasi-linear and the other is three-coordinate, actually it can be said there are two quasi linear complexes one of which coordinates to the oxygen of the ligand of the other complex. This bond is weak (2.710 Å) and it causes a slight increase in length of the C24–O4 bond rather than the other carbonyl bond length (Table 2). Two nitrate ions appear as counter ions and there is no Ag–ONO2 interactions.

There are two cation (+1) and one anion (−2) parts in the unit cell of complex **3** which are all silver(I)–ylide complexes.



Scheme 2 Different structures of complexes **1–6** in dichloromethane as solvent.

The configuration at the chiral carbon atoms in the cation and anion are RS and SS, respectively. In the anionic part, one formula unit comprises the asymmetric unit of the structure and silver atom being related by the inversion centre in the triclinic space group $P\bar{1}$ to form the whole molecule. The array about the silver(I) center is similar to complex **1** but herein nitrate coordinated through O10, *cf.* O4 in complex **1**, is a terminal ligand. The configuration of the cationic part is quite similar to analogous phosphorus ylide complexes reported to date.[1–4] The conformation about the molecular axis C1–C11 is almost eclipsed (Fig. 3). The coordination geometry at silver is essentially linear, although bond lengths and angles at the silver are slightly distorted (Tables 2 and 3).

There are no phosphorus analogs with the same substituents for complexes **2** and **3** to compare the corresponding bond length and angle values.

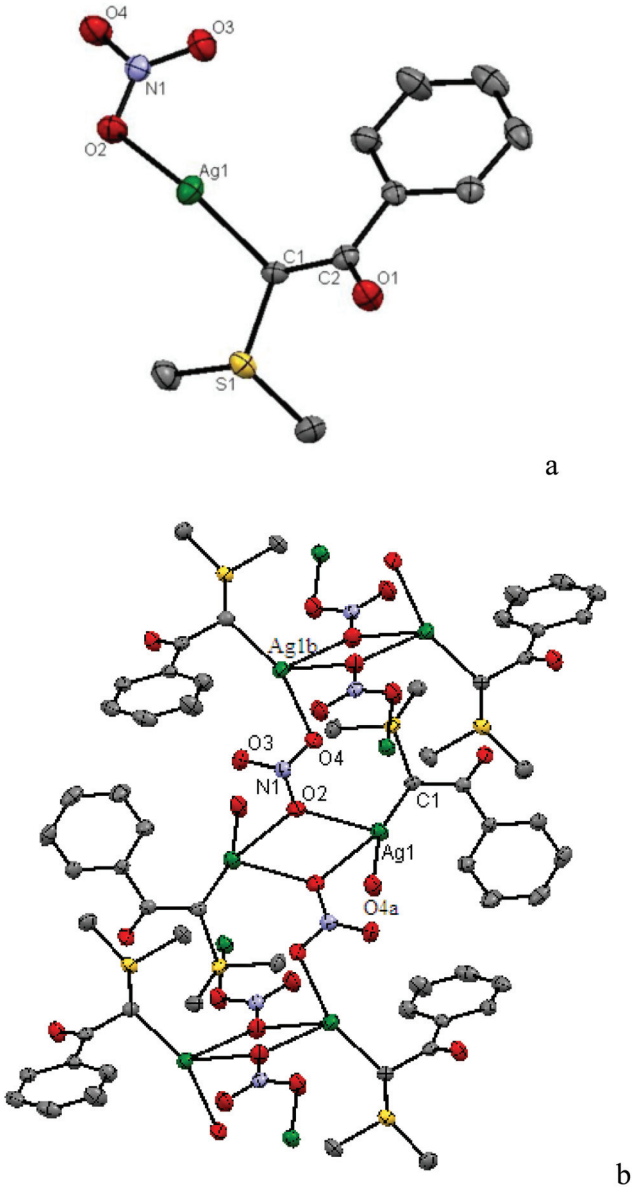


Fig. 1 ORTEP view of the X-ray crystal structure of **1**. (a) Asymmetric unit and (b) polymeric chain. The H atoms have been omitted for clarity. Symmetry code: [a]3/2 − *X*, 1/2 + *Y*, +*Z*; [b]3/2 − *X*, −1/2 + *Y*, +*Z*.

Although, we could not obtain good qualified single crystals to determine the true structures **4–6** by X-ray crystallography, nevertheless we investigated the spectroscopy and analytical data to suggest the possible structures. Infrared, ^{1}H- and ^{13}C-NMR spectra for complexes **4–6** are quite similar to complexes **1–3** so the analytical data helped us to predict possible structures for complexes **4–6.** Analytical data shows the stoichiometry between the silver(I) nitrate and ylide *p*-OMe (**4**) is 1 : 2 that is similar to complex **2**, a cationic binuclear, and 1 : 1 for ylides *p*-Me (**5**) and *p*-Br (**6**) which is similar to complex **1**, a two-dimensional polymer.

Antibacterial activity

Results from the antibacterial assessment of the samples are presented in Tables 4–10 and positive and negative controls

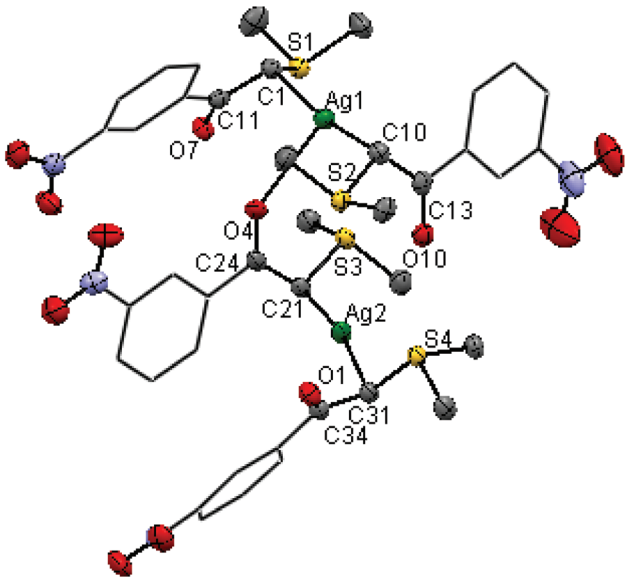


Fig. 2 ORTEP view of the X-ray crystal structure of **2**. The H atoms, tow nitrate counter ions and two water molecules have been omitted and the phenyl rings have been shown as wire form for clarity.

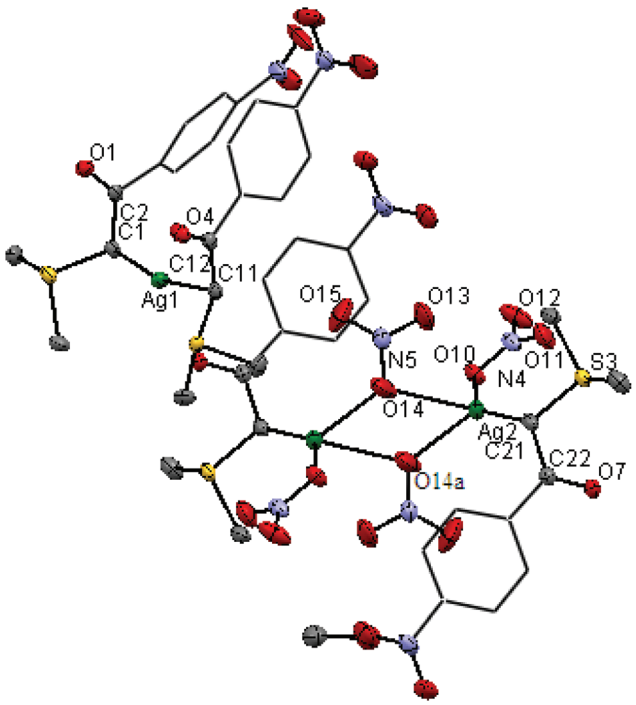


Fig. 3 ORTEP view of the X-ray crystal structure of **3**. The H atoms and two methanol molecules (solvent) have been omitted and the phenyl rings have been shown as wire form for clarity. Symmetry code: [a]1 − *X*, −*Y*, 1 − *Z*.

are shown in Table 11. The new complexes and their free ligands all displayed antibacterial activity against all bacteria tested especially on Gram negative ones. A comparative study of the growth inhibition zone values of ligands and its complexes indicate that complexes exhibit higher antibacterial activity than the free ligands. However, the presence of the

Table 1 Crystal data and refinement details for **1**, **2** and **3**

	1	**2**	**3**
Identification code	fa-assg	fa-agmGau	fa-asng
Formula	$C_{10}H_{12}AgNO_4S$	$C_{20}H_{24}N_3O_{10}S_2Ag$	$C_{62}H_{74}N_{10}O_{32}S_6Ag_4$
Formula weight	350.14	638.41	2095.15
Temperature (K)	130(2)	130(2)	130(2)
Wavelength (Å)	1.54184	1.54184	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 8.45746(19)	10.6373(4)	11.7239(4)
	b = 9.22142(17)	11.2057(3)	12.3813(3)
	c = 30.5647(7)	23.4336(6)	15.3188(4)
	α	80.762(2)	70.686(3)
	β	83.424(3)	68.015(3)
	γ	71.797(3)	88.073(2)
Volume (Å^3)	2383.73(9)	2612.88(14)	1935.54(10)
Z, calculated density (Mg m^{-3})	8, 1.951	4, 1.623	1, 1.797
Absorption coefficient (mm^{-1})	15.259	8.192	1.252
F(000)	1392	1296	1056.0
Crystal size (mm)	0.29 × 0.10 × 0.08	0.36 × 0.16 × 0.06	0.22 × 0.10 × 0.05
θ range for data collection (°)	2.88–76.80	3.83–77.17	2.85–30.06
Limiting indices	$-10 \le h \le 10$	$-13 \le h \le 12$	$-16 \le h \le 15$
	$-9 \le k \le 11$	$-13 \le k \le 14$	$-16 \le k \le 16$
	$-38 \le l \le 38$	$-28 \le l \le 29$	$-21 \le l \le 21$
Reflections collected/unique	22 299	26 669	21 179
	2518 [R(int) = 0.0401]	10 925 [R(int) = 0.0325]	10 020 [R(int) = 0.0299]
Completeness	99.97%	99.91%	99.88%
Absorption correction	Gaussian	Gaussian	Gaussian
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2518/0/156	10 925/62/659	10 020/12/524
Goodness-of-fit on F^2	1.095	1.064	1.039
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0278, wR_2 = 0.0663	R_1 = 0.0540, wR_2 = 0.1587	R_1 = 0.0356, wR_2 = 0.0705
R indices (all data)	R_1 = 0.0310, wR_2 = 0.0688	R_1 = 0.0609, wR_2 = 0.1665	R_1 = 0.0532, wR_2 = 0.0791
Largest diff. peak and hole (e Å^3)	0.670 and −0.81	2.77 and −1.84	0.68 and −0.66

Table 2 Selected bond lengths (Å) for **1**, **2** and **3** and comparison of complex **1** with triphenylphosphonium analog

1		[1]	**2**		**3**	
Ag1–C1	2.198(3)	2.219(9)	Ag1–C1	2.192(5)	Ag1–C1	2.215(2)
Ag1–O4[a]	2.303(2)	2.751(10)	Ag1–C10	2.202(5)	Ag1–C11	2.206(3)
Ag1–O2	2.590(2)	2.77(1)	Ag2–C21	2.177(5)	Ag2–C21	2.233(3)
C1–C2	1.454(4)	1.471(13)	Ag2–C31	2.177(5)	Ag2–O14	2.668(3)
C2–O1	1.239(3)	2.233(16)	C21–C24	1.445(8)	Ag2–O14[a]	2.414(2)
C1–S1	1.765(3)		C31–C34	1.464(6)	Ag2–O10	2.359(2)
O4–Ag1[b]	2.302(2)		C1–C11	1.447(7)	C1–C2	1.448(3)
N1–O2	1.256(3)		C10–C13	1.443(7)	C11–C12	1.449(4)
N1–O3	1.234(3)		C34–O1	1.224(6)	C21–C22	1.501(5)
N1–O4	1.267(3)	1.269(20)	C24–O4	1.249(6)	C22–O7	1.240(3)
			C13–O10	1.245(7)	C12–O4	1.236(3)
			C11–O7	1.243(6)	C2–O1	1.234(3)
			C21–S3	1.760(5)	C21–S3	1.759(3)
			C31–S4	1.768(5)	C1–S1	1.758(3)
			C10–S2	1.767(5)	N4–O10	1.256(3)
			C1–S1	1.766(5)	N4–O12	1.244(3)
					N5–O14	1.259(3)
					N5–O15	1.208(3)
					N5–O13	1.234(3)

See Fig. 1–3 for the atom numbering. [a]3/2 − X, 1/2 + Y, +Z; [b]3/2 − X, −1/2 + Y, +Z (**1**); [a]1 − X, −Y, 1 − Z (**3**)

different coordination modes does not exert much effect on the antibacterial activity of the tested complexes and almost all complexes exhibit equal antibacterial activity (Tables 5–10). Generally, antibacterial activities of the compounds are attributed mainly to their major components. However, today it is well known that the synergistic or antagonistic effect of one compound present in a minor percentage of a mixture has to be considered.[28] When antimicrobial activities of the tested samples were compared with some reference antibiotics, the inhibitory potency of the tested ligands and chiefly complexes was found to be remarkable (Tables 4–11). Although all bacteria tested are resistant to penicillin and *E. coli* to gentamicin, the antibacterial effects of all ligands and their complexes were higher than those of antibiotics on these bacteria. The complexes showed more activity against some bacteria under identical experimental conditions. This would suggest that the structure of the complexes may reduce the polarity of the metal ion mainly. In addition, silver(I) ions reportedly adhere to the negatively charged bacteria cell walls and change the cell wall permeability. This action coupled with protein denaturation induces cell lyses and death.[29] The antimicrobial activity of silver ion is also related to its ability to modify DNA replication mechanisms as well as to cause abnormalities in the size, cytoplasmic contents, cell membrane, and outer cell layers of sensitive cells.[30] Overall the present study revealed Gram negative bacteria to be more susceptible to the antibacterial effects of silver(I) complexes than Gram positives, presumably due to their thinner wall, which may allow more rapid absorption of the ions into the cell.[31,32] The above results indicate that the studied complexes may be used in the

Table 3 Selected bond angles (°) for **1**, **2** and **3**

1		**2**		**3**	
O4[a]–Ag1–O2	83.46(7)	C1–Ag1–C10	168.19(19)	C1–Ag1–C11	166.14(9)
O4[a]–Ag1–C1	158.88(9)	C11–C1–Ag1–	102.2(3)	C2–C1–Ag1	99.95(16)
C1–Ag1–O2	113.00(8)	C13–C10–Ag1	104.1(3)	C12–C11–Ag1	99.61(16)
Ag1–O2–N1	116.60(16)	S1–C1–Ag1	111.0(2)	S1–C1–Ag1	106.22(12)
O3–N1–O2	120.8(2)	S2–C10–Ag1	109.5(2)	S2–C11–Ag1	112.06(13)
O3–N1–O4	120.4(2)	O7–C11–C1	122.1(4)	O14–Ag2–O	106.76(10)
O4–N1–O2	118.8(2)	O10–C13–C10	122.6(5)	C21–Ag2–O10	142.08(9)
S1–C1–Ag1	108.50(12)	C21–Ag2–C31	167.05(18)	C21–Ag2–O14	103.74(9)
O1–C2–C1	123.0(2)	C24–C21–Ag2	99.2(3)	C21–Ag2–O14[a]	133.70(9)
C2–C1–Ag1	107.18(17)	C34–C31–Ag2	107.0(3)	O14[a]–Ag2–O14	69.54(11)
N1–O4–Ag1[b]	111.84(16)	S3–C21–Ag2	113.2(2)	N4–O10–Ag2	109.7(3)
		S4–C31–Ag2	106.3(2)	N5–O15–Ag2	117.9(3)
		O4–C24–C21	123.9(4)	S3–C20–Ag2	106.72(18)
		O1–C34–C31	123.4(5)	C21–C20–Ag2	105.2(3)

Table 4 Antibacterial activity of free ligands **1–6**

	Inhibition zone (mm)					
Compounds	Concentration	*P. vulgaris* (−)	*E. coli* (−)	*B. cereus* (+)	*S. aureus* (+)	*B. megaterium* (+)	*S. marcescens* (−)
Ligand **1**	1 (mg ml^{-1})	9 ± 0.22[a]	7 ± 0.18	7 ± 0.00	8 ± 0.00	9 ± 0.12[a]	10 ± 0.24[a]
	0.1 (mg ml^{-1})	7 ± 0.14[b]	Na	Na	Na	7 ± 0.28[b]	8 ± 0.14[b]
	0.01 (mg ml^{-1})	Na	Na	Na	Na	Na	Na
Ligand **2**	1 (mg ml^{-1})	8 ± 0.24[a]	10 ± 0.15[a]	8 ± 0.12	7 ± 0.10	8 ± 0.00	11 ± 0.24[a]
	0.1 (mg ml^{-1})	7 ± 0.18[b]	7 ± 0.14[b]	Na	Na	Na	9 ± 0.14[b]
	0.01 (mg ml^{-1})	Na	Na	Na	Na	Na	Na
Ligand **3**	1 (mg ml^{-1})	9 ± 0.16[a]	7 ± 0.26	8 ± 0.15	9 ± 0.00[a]	7 ± 0.22	8 ± 0.24[a]
	0.1 (mg ml^{-1})	8 ± 0.15[b]	Na	Na	7 ± 0.24[b]	Na	7 ± 0.18[b]
	0.01 (mg ml^{-1})	Na	Na	Na	Na	Na	Na
Ligand **4**	1 (mg ml^{-1})	10 ± 0.15[a]	8 ± 0.26	7 ± 0.15	7 ± 0.33	Na	11 ± 0.24[a]
	0.1 (mg ml^{-1})	8 ± 0.33[b]	Na	Na	Na	Na	9 ± 0.18[b]
	0.01 (mg ml^{-1})	Na	Na	Na	Na	Na	7 ± 0.18[c]
Ligand **5**	1 (mg ml^{-1})	8 ± 0.16	9 ± 0.33[a]	8 ± 0.15	7 ± 0.00	9 ± 0.33[a]	9 ± 0.24[a]
	0.1 (mg ml^{-1})	Na	7 ± 0.00[b]	Na	Na	8 ± 0.26[b]	7 ± 0.18[b]
	0.01 (mg ml^{-1})	Na	Na	Na	Na	Na	Na
Ligand **6**	1(mg ml^{-1})	9 ± 0.28[a]	8 ± 0.45[a]	7 ± 0.18	8 ± 0.00	8 ± 0.33[a]	10 ± 0.12[a]
	0.1(mg ml^{-1})	8 ± 0.14[b]	7 ± 0.10[b]	Na	Na	7 ± 0.14[b]	9 ± 0.36[b]
	0.01(mg ml^{-1})	7 ± 0.18[c]	Na	Na	Na	Na	Na

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

treatment of diseases caused by the bacteria tested. Further studies are needed to evaluate the *in vivo* potential of these compounds in animal models.

Experimental

All solvents were reagent grade and used without further purification. NMR spectra were obtained on 400 MHz Varian MR400 and 90 MHz Jeol spectrometers in $CDCl_3$ and DMSO-d_6 as the solvent. Chemical shifts (δ) are reported relative to internal TMS (^{1}H and ^{13}C). Melting points were measured on a Stuart SMPI apparatus. Elemental analysis for C, H and N were performed using a Perkin-Elmer 2400 series analyzer. Fourier transform infrared spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets.

Preparation of ligands

The synthesis and infrared, ^{1}H and ^{13}C NMR spectroscopic characterization of all ligands except the new ylide, $Me_2SCHC(O)C_6H_4$-*m*-NO_2, have been reported previously[33–35] and ESI.†

Table 5 Antibacterial activity of complex **1**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.22^{a}	10 ± 0.14^{b}	8 ± 0.16^{c}
E. coli (−)	11 ± 0.34^{a}	8 ± 0.12^{b}	Na
B. cereus (+)	12 ± 0.24^{a}	10 ± 0.18^{b}	7 ± 0.14^{c}
S. aureus (+)	11 ± 0.18^{a}	10 ± 0.24^{b}	8 ± 0.22^{c}
B. megaterium (+)	10 ± 0.16^{a}	9 ± 0.28^{b}	7 ± 0.12^{c}
S. marcescens (−)	13 ± 0.18^{a}	11 ± 0.33^{b}	8 ± 0.00^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Table 6 Antibacterial activity of complex **2**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.22^{a}	9 ± 0.14^{b}	8 ± 0.16^{c}
E. coli (−)	13 ± 0.34^{a}	10 ± 0.22^{b}	Na
B. cereus (+)	10 ± 0.24^{a}	10 ± 0.18^{b}	7 ± 0.14^{c}
S. aureus (+)	11 ± 0.18^{a}	9 ± 0.24^{b}	8 ± 0.22^{c}
B. megaterium (+)	10 ± 0.16^{a}	7 ± 0.12^{b}	Na
S. marcescens (−)	14 ± 0.18^{a}	11 ± 0.33^{b}	8 ± 0.00^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Table 7 Antibacterial activity of complex **3**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.34^{a}	10 ± 0.15^{b}	8 ± 0.11^{c}
E. coli (−)	12 ± 0.45^{a}	10 ± 0.18^{b}	7 ± 0.14^{c}
B. cereus (+)	10 ± 0.22^{a}	9 ± 0.18^{b}	Na
S. aureus (+)	11 ± 0.28^{a}	10 ± 0.4^{b}	9 ± 0.16^{c}
B. megaterium (+)	10 ± 0.18^{a}	9 ± 0.14^{b}	7 ± 0.00^{c}
S. marcescens (−)	12 ± 0.12^{a}	10 ± 0.24^{b}	7 ± 0.11^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Preparation of [$Me_2SCHC(O)C_6H_4$-*m*-NO_2]. To an acetone solution (10 ml) of dimethylsulfide (0.062 g, 1.00 mmol) was added 2-bromo-3′-nitroacetophenone (0.244 g, 1.00 mmol) and the mixture was stirred for 12 h. The solid product (sulfonium salt) was isolated by filtration, washed with ether and dried under reduced pressure. Further treatment with aqueous 10% NaOH solution led to elimination of HBr, giving the free ligand. Yield 0.168 g, 75%. Anal. Calc for $C_{10}H_{11}O_3SN$: C, 53.32; H, 4.92. Found: C, 53.01; H, 4.85. M.p. 110–112 C. IR (KBr disk): ν (cm^{-1}) 1583 (C═O). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.98 (s, 6H, $S(CH_3)_2$); 4.36 (1H, CH); 7.41 (m, 2H, Ph); 8.12 (dd, $^{3}J_{HH}$ = 3.6 Hz, 1H, Ph); 8.54 (s, 1H, Ph). ^{13}C-NMR ($CDCl_3$, ppm): δ 28.28 (s, $S(CH_3)_2$); 55.40 (s, CH); 120.72 (s, Ph); 123.20

Table 8 Antibacterial activity of complex **4**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.43^{a}	10 ± 0.16^{b}	8 ± 0.16^{c}
E. coli (−)	12 ± 0.33^{a}	8 ± 0.18^{b}	8 ± 0.18^{c}
B. cereus (+)	10 ± 0.16^{a}	9 ± 0.12^{b}	7 ± 0.11^{c}
S. aureus (+)	10 ± 0.18^{a}	10 ± 0.22^{b}	9 ± 0.14^{c}
B. megaterium (+)	9 ± 0.24^{a}	Na	Na
S. marcescens (−)	14 ± 0.34^{a}	11^{b} ± 0.22^{b}	9 ± 0.18^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Table 9 Antibacterial activity of complex **5**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.22^{a}	10 ± 0.38^{b}	8 ± 0.12^{c}
E. coli (−)	12 ± 0.28^{a}	8 ± 0.15^{b}	Na
B. cereus (+)	10 ± 0.12^{a}	7 ± 0.00^{b}	Na
S. aureus (+)	11 ± 0.17^{a}	10 ± 0.18^{b}	9 ± 0.22^{c}
B. megaterium (+)	12 ± 0.33^{a}	9 ± 0.24^{b}	Na
S. marcescens (−)	12 ± 0.28^{a}	10 ± 0.33^{b}	9 ± 0.14^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Table 10 Antibacterial activity of complex **6**

Microorganism	Inhibition zone (mm)		
	Concentration (1 mg ml^{-1})	Concentration (0.1 mg ml^{-1})	Concentration (0.01 mg ml^{-1})
P. vulgaris (−)	12 ± 0.34^{a}	10 ± 0.22^{b}	8 ± 0.11^{c}
E. coli (−)	12 ± 0.56^{a}	8 ± 0.16^{b}	7 ± 0.00^{c}
B. cereus (+)	10 ± 0.22^{a}	7 ± 0.00^{b}	Na
S. aureus (+)	11 ± 0.18^{a}	10 ± 0.14^{b}	8 ± 0.18^{c}
B. megaterium (+)	12 ± 0.25^{a}	9 ± 0.12^{b}	Na
S. marcescens (−)	13 ± 0.28^{a}	10 ± 0.24^{b}	7 ± 0.00^{c}

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for each bacterium in different concentrations) are significantly different ($P < 0.05$). Na: Not active.

Table 11 Antibacterial activities of antibiotics as positive controls and DMSO as negative control

	Inhibition zone (mm)				
	Positive controls				Negative control
Microorganism	Gentamicin	Penicillin	Nitrofurantion	Neomycin	DMSO
P. vulgaris (−)	30 ± 0.14	Na	15 ± 0.22	22 ± 0.16	Na
E. coli (−)	Na	Na	25 ± 0.22	20 ± 0.33	Na
B. cereus (+)	25 ± 0.18	Na	10 ± 0.12	20 ± 0.36	Na
S. aureus (+)	35 ± 0.24	Na	30 ± 0.34	25 ± 0.45	Na
B. megaterium (+)	25 ± 0.33	Na	20 ± 0.28	20 ± 0.55	Na
S. marcescens (−)	27 ± 0.18	Na	18 ± 0.14	22 ± 0.28	Na

Experiment was performed in triplicate and expressed as mean ± SD. Na: Not active.

(s, Ph); 128.38 (s, Ph); 131.98 (s, Ph); 142.29 (s, Ph); 147.55 (s, Ph); 178.05 (s, CO).

Preparation of complex $[AgNO_3(Me_2SCHC(O)C_6H_5)]_n$ (1). To a dichloromethane solution (15 ml) of $AgNO_3$ (0.169 g, 1.00 mmol) was added a methanolic solution (10 ml) of ylide $Me_2SCHC(O)C_6H_5$ (0.180 g, 1.0 mmol). The solution was protected from light with aluminum foil and stirred at room temperature. After 3–4 h the mixture was filtered through Celite and the filtrate concentrated to 3–5 ml. Addition of petroleum ether (15–30 ml) precipitated the product.

Yield 0.213 g, 61%. Anal. Calc for $AgNO_4SC_{10}H_{12}$: C, 34.30; H, 3.45; N, 4.00. Found: C, 34.06; H, 3.50; N, 3.89. Decomposition at 120–122 °C. IR (KBr disk): ν (cm^{-1}) 1668 (CO). ^{1}H-NMR ($CDCl_3$, ppm): δ 2.86 (s, 6H, $S(CH_3)_2$); 4.69 (s, 1H, CH); 7.32 (dd, $^3J_{HH}$ = 7.8 Hz, 2H, Ph); 7.41 (dd, $^3J_{HH}$ = 7.8 Hz, 1H, Ph); 7.84 (d, $^3J_{HH}$ = 8.0 Hz, 3H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 28.28 (s, $S(CH_3)_2$); 54.12 (s, CH); 127.11 (s, Ph(*p*)); 128.57 (s, Ph(*m*)); 131.66 (s, Ph(*o*)); 138.15 (s, Ph(*i*)); 188.74 (s, CO).

Preparation of complex $[Ag(Me_2SCHC(O)C_6H_4\text{-}m\text{-}NO_2)_2]_2(NO_3)_2\cdot 2H_2O$ (2). Complex **2** was prepared following the same method used for **1**. Thus, $AgNO_3$ (0.168 g, 1.00 mmol) was reacted with ylide $Me_2SCHC(O)C_6H_4$-*m*-NO_2 (0.448 g, 2.0 mmol) giving **2**.

Yield 0.415 g, 67%. Anal. Calc for $C_{20}H_{22}AgN_3O_9S_2$: C, 38.72; H, 3.57; N, 6.77. Found: C, 38.59; H, 3.64; N, 6.65. M.p. 168–170 °C. IR (KBr disk): ν (cm^{-1}) 1686 (CO). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.84 (s, 6H, $S(CH_3)_2$); 5.04 (br, 1H, CH); 7.67 (m, 2H, Ph); 8.20 (m, 1H, Ph); 8.54 (s, 1H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 28.36 (s, $S(CH_3)_2$); 55.15 (s, CH); 121.17 (s, Ph)); 125.42 (s, Ph); 130.10 (s, Ph)); 133.10 (s, Ph); 139.93 (s, Ph); 148.04 (s, Ph); 183.39 (s, CO).

Preparation of complex $[Ag(Me_2SCHC(O)C_6H_4\text{-}p\text{-}NO_2)_2]_2[\{AgNO_3(\mu\text{-}NO_3)(Me_2SCHC(O)C_6H_4\text{-}p\text{-}NO_2)\}_2]\cdot 2CH_3OH$ (3). Complex **3** was prepared following the same method used for **1**. Thus, $AgNO_3$ (0.336 g, 2.00 mmol) was reacted with ylide $Me_2SCHC(O)C_6H_4$-*p*-NO_2 (0.672 g, 3.0 mmol) giving **3**.

Yield 0.731 g, 72%. Anal. Calc for $Ag_4N_{10}O_{30}S_6C_{60}H_{66}$: C, 35.48; H, 3.28; N, 6.90. Found: C, 35.12; H, 3.35; N, 6.74. M.p. 109–110 °C. IR (KBr disk): ν (cm^{-1}) 1675 (CO). ^{1}H-NMR ($CDCl_3$, ppm): δ 3.02 (s, 6H, $S(CH_3)_2$); 4.40 (s, 1H, CH); 7.88 (d, $^3J_{HH}$ = 8.9 Hz, 2H, Ph); 8.19 (d, $^3J_{HH}$ = 8.9 Hz, 2H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 28.05 (s, $S(CH_3)_2$); 57.34 (s, CH); 123.11 (s, Ph(*m*)); 127.46 (s, Ph(*o*)); 144.96 (s, Ph(*i*)); 147.95 (s, Ph(*p*)); 180.19 (s, CO).

Preparation of complex $[Ag(Me_2SCHC(O)C_6H_4\text{-}p\text{-}OMe)_2]NO_3$ (4). Complex **4** was prepared following the same method used for **1**. Thus, $AgNO_3$ (0.168 g, 1.00 mmol) was reacted with ylide $Me_2SCHC(O)C_6H_4$-*p*-OMe (0.420 g, 2.0 mmol) giving **4**.

Yield 0.407 g, 69%. Anal. Calc for $AgNO_7S_2C_{22}H_{28}$: C, 44.75; H, 4.78; N, 2.37. Found: C, 45.25; H, 5.0; N, 2.3. Decomposition at 136–138 °C. IR (KBr disk): ν (cm^{-1}) 1661 (CO). ^{1}H-NMR ($CDCl_3$, ppm): δ 3.77 (s, 3H, OCH_3); 2.75 (s, 6H, $S(CH_3)_2$); 4.78 (s, 1H, CH); 6.70 (d, $^3J_{HH}$ = 8.9 Hz, 2H, Ph); 7.79 (d, $^3J_{HH}$ = 8.9 Hz, 2H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 28.43 (s, $S(CH_3)_2$); 53.75 (s, CH); 55.73 (s, OCH_3); 113.64 (s, Ph(*p*)); 129.00 (s, Ph(*m*)); 130.83 (s, Ph(*o*)); 162.01 (s, Ph(*i*)); 187.94 (s, CO).

Preparation of complex $[AgNO_3(Me_2SCHC(O)C_6H_4\text{-}p\text{-}Me)]_n$ (5). Complex **5** was prepared following the same method used for **1**. Thus, $AgNO_3$ (0.168 g, 1.00 mmol) was reacted with ylide $Me_2SCHC(O)C_6H_4$-*p*-Me (0.194 g, 1.0 mmol) giving **5**.

Yield 0.209 g, 75%. Anal. Calc for $Ag_2N_2O_8S_2C_{22}H_{28}$: C, 36.28; H, 3.87; N, 3.58. Found: C, 36.9; H, 3.80; N, 3.80. M.p. 111–112 °C. IR (KBr disk): ν (cm^{-1}) 1671 (CO). ^{1}H-NMR ($CDCl_3$, ppm): δ 2.30 (s, 3H, CH_3); 2.76 (s, 6H, $S(CH_3)_2$); 4.84 (s, 1H, CH); 7.16 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph); 7.74 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 21.66 (s, CH_3); 26.98 (s, $S(CH_3)_2$); 52.50 (s, CH); 128.20 (s, Ph(*p*)); 129.52 (s, Ph(*m*)); 132.45 (s, Ph(*o*)); 144.20 (s, Ph(*i*)); 192.97 (s, CO).

Preparation of complex $[AgNO_3Me_2SCHC(O)C_6H_4\text{-}p\text{-}Br]$ (6). Complex **6** was prepared following the same method used for **1**. Thus, $AgNO_3$ (0.168 g, 1.00 mmol) was reacted with ylide $Me_2SCHC(O)C_6H_4$-*p*-Br (0.259 g, 1.0 mmol) giving **6**.

Yield 0.334 g, 78%. Anal. Calc for $AgNO_4BrSC_{10}H_{11}$: C, 27.99; H, 2.58; N, 3.26. Found: C, 28.5; H, 2.7; N, 2.90. Decomp. 114–117 °C. IR (KBr disk): ν (cm^{-1}) 1678 (CO). ^{1}H-NMR ($CDCl_3$, ppm): δ; 2.81 (s, 6H, $S(CH_3)_2$); 4.80 (s, 1H, CH); 7.37 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph); 7.68 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph). ^{13}C-NMR (DMSO-d_6, ppm): δ 28.20 (s, $S(CH_3)_2$), 53.68 (s, CH), 125.31 (s, Ph(*m*)); 129.16 (s, Ph(*p*)); 131.49 (s, Ph(*i*)); 137.08 (s, Ph(*o*)); 187.29 (s, CO).

X-ray crystallography

2.2. X-ray crystallography

Data collection from suitable crystals of **1**, **2** and **3** was performed on an Oxford Diffraction single-crystal X-ray diffractometer using mirror monochromated Cu and Mo Kα radiation (1.54184 and 0.71073 Å, respectively) at 130 K (Table 1). Gaussian absorption corrections were carried out using a multifaceted crystal model, using CrysAlisPro.[36] All three structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 crystallographic package.[37,38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding model, with isotropic displacement parameters.

Antibacterial activity

The potential antibacterial effects of the complexes were investigated by agar disc diffusion method against three Gram positive bacteria, namely *Bacillus cereus* (PTCC 1247), *Staphylococcus aureus* (Wild) and *Bacillus megaterium* (PTCC 1017), and 3 Gram negative bacteria, namely *Escherichia coli* (Wild), *Proteus vulgaris* (PTCC 1079), and *Serratia marcescens* (PTCC 1111).[39] The complexes were dissolved in DMSO to a final concentration of 1 mg ml^{-1} and then sterilized by filtration using 0.45 μm Millipore. All tests were carried out using 10 ml of suspension containing 1.5×10^8 bacteria per ml and spread on nutrient agar medium. Negative controls were prepared by using DMSO. Gentamycin, penicillin, neomycin and nitrofurantoin were used as positive reference standards. The diameters of inhibition zones generated by the complexes were measured.

2.4. Statistical analysis

All data, for both antibacterial tests, are the average of triplicate analyses. Analysis of variance was performed by Excel and SPSS procedures Statistical analysis was performed using Student's *t*-test, and p value < 0.05 was regarded as significant.

Conclusion

The present study describes the synthesis and characterization of some novel and unexpected silver(I) complexes of carbonyl-stabilized sulfonium ylides. Unlike the phosphonium ylide complexes that coordinate to ligands only through the carbon atom and always show a linear geometry, sulfonium analogs can form various coordination geometries. On the basis of the physico-chemical, spectroscopic and X-ray crystallographic data, it is clear that the sulfonium ylide ligands described herein exhibit monodentate C-coordination to the metal centers in all compounds except complex **2**. In this complex, the related ligand coordinates to two silver atoms through the carbon of the carbanion and the oxygen of the carbonyl group. Our results clearly demonstrated that silver(I) complexes exhibit antibacterial properties that might be helpful as an alternative system of medicine. However, possible deleterious side-effects of these compounds on human health must be further investigated. Future research will involve studies on possible modification of these complexes to increase their antibacterial activity.

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Notes and references

1 J. Vicente, M. T. Chicote, J. Femandez-Baeza, J. Martin, I. Saura-Llamas, J. Turpin and P. G. Jones, *J. Organomet. Chem.*, 1987, **331**, 409.
2 J. Vicente, M. T. Chicote, I. Saura-Llamas and J. Turpin, *J. Chem. Educ.*, 1993, **70**, 163.
3 K. Karami and O. Buyukgungor, *J. Coord. Chem.*, 2009, **62**, 2949.
4 S. J. Sabounchei, M. Sarlakifar, S. Salehzadeh, M. Bayat, M. Pourshahbaz and H. R. Khavasi, *Polyhedron*, 2012, **38**, 131.
5 J. Stephen Clark, *Nitrogen, Oxygen and Sulfur Ylide Chemistry, A Practical Approach in Chemistry*, Oxford University Press, Britain, 2002.
6 S. Deuerlein, D. Leusser, U. Flierler, H. Ott and D. Stalke, *Organometallics*, 2008, **27**, 2306.
7 I. Kawafune and G. Matsubayashi, *Inorg. Chim. Acta*, 1983, **70**, 1.
8 G. Matsubayashi, I. Kawafune, T. Tanaka, S. Nishigaki and K. Nakatsu, *J. Organomet. Chem.*, 1980, **187**, 113.
9 F. D. Lowry, *J. Clin. Invest.*, 2003, **111**, 1265.
10 H. Richet, J. Mohammed, L. C. McDonald and W. R. Jarvis, *Emerging Infect. Dis.*, 2001, **7**, 319.
11 D. J. Payne, M. N. Gwynn, D. J. Holmes and M. Rosenberg, *Methods Mol. Biol.*, 2004, **266**, 231.
12 R. M. Slawson, M. I. Van Dyke, H. Lee and J. T. Trevors, *Plasmid*, 1992, **27**, 72.
13 G. J. Zhao and S. E. Stevens, *BioMetals*, 1998, **11**, 27.
14 A. Melaiye, Z. H. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier and W. J. Youngs, *J. Am. Chem. Soc.*, 2005, **127**, 2285.
15 S. Abuskhuna, J. Briody, M. McCann, M. Devereux, K. Kavanagh, J. B. Fontecha and V. McKee, *Polyhedron*, 2004, **23**, 1249.
16 M. A. M. Abu-Youssef, V. Langer and L. Öhrström, *Dalton Trans.*, 2006, 2542.
17 I. Sondi and B. Salopek-Sondi, *J. Colloid Interface Sci.*, 2004, **275**(1), 177.

18 A. R. Shahverdi, A. Fakhimi, H. R. Shahverdi and S. Minaian, *Nanomed.: Nanotechnol., Biol. Med.*, 2007, **3**(2), 168.
19 M. Saravanan and A. Nanda, *Colloids Surf., B*, 2010, **77**, 214.
20 S. A. Bishara, C. Michel, N. H. Shady and A. D. Saad, *Burns*, 2007, **33**, 148.
21 S. Djokić, *ECS Trans.*, 2008, **11**, 1.
22 M. J. Stillman, A. Presta, Z. Gui and D. T. Jiang, *Met.-Based Drugs*, 1994, **1**, 375.
23 W. L. K. Menno and H. K. Leo, *Polymers*, 2011, **3**, 340.
24 X. Chen and H. J. Schluesener, *Toxicol. Lett.*, 2008, **176**(1), 1.
25 J. Buckle and P. G. Harrison, *J. Organomet. Chem.*, 1973, **49**, C17.
26 R. Uson, J. Forniés, R. Navarro, P. Espinet and C. Mendívil, *J. Organomet. Chem.*, 1985, **290**, 125.
27 K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1185.
28 S. Burt, *Int. J. Food Microbiol.*, 2004, **94**, 223.
29 Y. E. Lin, R. D. Vidic, J. E. Stout and V. L. Yu, *Water Res.*, 1996, **30**, 1905.
30 A. D. Russell and W. B. Hugo, *Prog. Med. Chem.*, 1994, **31**, 351.
31 J. M. Schierholz, L. J. Lucas, A. Rump and G. Pulvere, *J. Hosp. Infect.*, 1998, **40**, 257.
32 J. E. Gray, P. R. Norton, R. Alnouno, C. L. Marolda, M. A. Valvano and K. Griffiths, *Biomaterials*, 2003, **24**, 2759.
33 S. J. Sabounchei, F. Akhlaghi Bagherjeri, C. Boskovic, R. W. Gable, R. Karamian and M. Asadbegy, *J. Mol. Struct*, DOI: 10.1016/j.molstruc.2012.10.051.
34 S. J. Sabounchei, F. Akhlaghi Bagherjeri, C. Boskovic, R. W. Gable, R. Karamian and M. Asadbegy, *Polyhedron*, Decision in Process with manuscript number: POLY-D-12-00945R1.
35 S. J. Sabounchei, F. Akhlaghi Bagherjeri, C. Boskovic and R. W. Gable, *Inorg. Chim. Acta*, Required Reviews Completed with manuscript number: ICA-D-12-00692.
36 CrysAlisPro, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171.NET) (compiled Oct 27 2011,15:02:11).
37 G. M. Sheldrick, SHELXL, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.
38 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.*, 2009, **42**, 339.
39 O. Awoyinka, *J. Med. Plants Res.*, 2007, **3**, 63.