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Binuclear mercury(II) complexes of sulfonium ylides: Synthesis, structural characterization and anti-bacterial activity

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HIGHLIGHTS

- The binuclear mercury complexes of sulfonium ylides are structurally characterized for the first time.
- IR, ^{1}H- and ^{13}C NMR spectroscopy demonstrates C-coordination of the ylide to the metal.
- There is an asymmetric halide-bridge structure similar to binuclear phosphonium analogs.
- The Hg—C bond length in mercury(II) complexes sulfonium ylides is less than phosphonium analogs.
- All complexes display antibacterial activity against the bacteria tested especially on Gram positive ones.

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ABSTRACT

Reaction of α-keto stabilized sulfonium ylides $(Me)_2SCHC(O)C_6H_4R$ (R = *p*-Me (*a*); *p*-Cl (*b*)) with HgX_2 (X = Cl, Br and I) in equimolar ratios using methanol as solvent leads to binuclear products of the type $[HgX_2(ylide)]_2$ (X = Cl (**1**), Br (**2**) and I (**3**)). Single crystal X-ray diffraction analysis reveals the presence of unexpected asymmetric halide-bridged dinuclear structures for **1a** and **2b**. Characterization of the compounds by IR, ^{1}H- and ^{13}C NMR spectroscopy confirmed coordination of the ylide to the metal through the carbon atom. In addition, the antibacterial effects of DMSO-solutions of the complexes were investigated by the disc diffusion method against three Gram positive and three negative bacteria. All complexes represent antibacterial activity against these bacteria with high levels of inhibitory potency exhibited against the Gram-positive species.

1. Introduction

Sulfur ylides $R_2S{=}C(R')(R'')$ are very reactive species with interesting applications in organic synthesis [1–4]. In addition they can behave as ligands, since the carbanion located at the Cα of the ylide is able to donate electron density to a transition metal [5,6]. In the case of α-keto stabilized ylides, $R_2S{=}C(R')CO(R'')$, various binding modes have been reported due to their ambidentate character (Scheme 1) [7,8].

Far more widely studied than sulfonium ylides, are their phosphorus analogs, with the configuration of mercury(II) halides complexes with phosphonium ylides well-known and extensively studied [9,10]. However the configuration of the analogous sulfonium ylide complexes is to date unknown as such species are yet to be structurally characterized.

The synthesis of complexes derived from sulfonium ylides and mercury(II) halides was first reported in 1975 by Weleski et al. [11], with a symmetric halide-bridge binuclear structure proposed. In 1984, Tewari and Awasthi [12] reported the synthesis of a series of transition metal halide complexes with various sulfonium ylides without further characterization.

Antibacterial agents are often co-administered with an inhibitor that deactivates the bacteria's resistance mechanism and increases the effectiveness of the antibacterial agents. The development of compounds with the ability to inhibit bacterial growth have been of great interest in recent years due to their potential use both in hospital equipment and in everyday items such as soaps, detergents, health and skincare products and household cleaners. Inorganic antibacterial materials have several advantages over traditionally used organic compounds, including chemical stability, thermal resistance, safety to the user, long lasting action period, etc. [13]. Bacterial resistance is a major drawback in chemotherapy of infectious disease [14]. The emergence, and observed increase,

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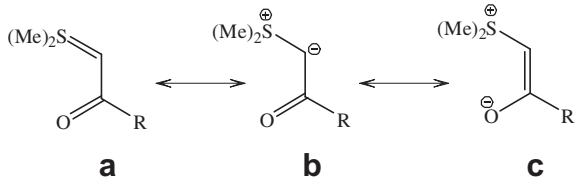


Scheme 1. The canonical forms of $(Me)_2SCHC(O)C_6H_4R$ (*R* = *p*-Me (*a*); *p*-Cl (*b*)).

of bacterial resistance to antibiotics has become a serious health problem worldwide, resulting in the diminution of the effectiveness of a number of important drugs. As a result there has been increasing interest in the use of inhibitors of antibiotic resistance for combination therapy [15–18].

Here we present the preparation, spectroscopic and structural characterization of binuclear mercury(II) complexes with sulfonium ylides, together with an in vitro determination of their antibacterial activity. This includes the first instance of sulfur ylide complexes of mercury(II) halides being structurally characterized, the complexes having an unexpected asymmetric halide-bridged dinuclear structure. The structures are compared with those of the analogous phosphorus ylides.

2. Experimental

2.1. Physical measurements and materials

All solvents were reagent grade and used without further purifications. NMR spectra were obtained on 400 MHz Varian MR400 and 90 MHz Jeol spectrometers in DMSO-d_6 and $CDCl_3$ 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.

2.2. X-ray crystallography

Data collection from suitable crystals of **1a** and **2b** was performed on an Oxford Diffraction single-crystal X-ray diffractometer using mirror monochromated Mo Kα radiation (0.71073 Å) at 130 K (Table 1). Gaussian absorption corrections were carried out using a multifaceted crystal model, using CrysAlisPro [19]. 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 [20,21]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding model, with isotropic displacement parameters.

2.3. Antibacterial activity

The potential antibacterial effects of the Hg(II) complexes were investigated by disc diffusion method against three Gram positive bacteria, namely *Bacillus cereus* (PTCC 1247), *Staphylococcus aureus* (Wild) and *Bacillus megaterium* (PTCC 1017), and three Gram negative bacteria, namely *Escherichia coli* (Wild), *Proteus vulgaris* (PTCC 1079), and *Serratia marcescens* (PTCC 1111) [22]. 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 using 10 ml of suspension containing 1.5×10^8 bacteria/ml and spread on nutrient agar medium. Negative controls were prepared by using DMSO. Gentamicin, Penicillin, Neomycin and Nitrofurantoin were used as positive reference standards.

Table 1
Crystal data and refinement details for complexes **1a** and **2b.**

	1a	**2b**
Identification code	Fa-lsmg	Fa-rslg
Formula	C_{22} H_{28} Cl_4 Hg_2 O_2 S_2	C_{20} H_{22} Br_4 Cl_2 Hg_2 O_2 S_2
Formula weight	931.54	1150.22
Temperature (K)	130(2)	130(2)
Wavelength (Å)	0.71073	0.71073
Crystal system space group	Triclinic $P-1$	Triclinic $P-1$
Unit cell dimensions	a = 8.0210(4)	8.4703(5)
	b = 8.3249(4)	8.6912(4)
	c = 10.8031(5)	10.5054(5)
	α = 99.745(4)	97.513(4)
	β = 103.853(4)	112.188(5)
	γ = 104.519(4)	90.483(4)
Volume (Å^3)	657.53(5)	708.55(6)
Z, Calculated density (Mg/m^3)	1, 2.353	1, 2.696
Absorption coefficient (mm^{-1})	12.245	16.813
F(000)	436	524.0
Crystal size (mm)	0.51 × 0.26 × 0.19	0.23 × 0.20 × 0.06
θ Range for data collection (°)	2.87–29.99	2.93–29.99
Limiting indices	$-11 \leqslant h \leqslant 11$	$-11 \leqslant h \leqslant 11$
	$-11 \leqslant k \leqslant 11$	$-9 \leqslant k \leqslant 12$
	$-11 \leqslant l \leqslant 15$	$-14 \leqslant l \leqslant 13$
Reflections collected/ unique	3398	3657
	3172 [R(int) = 0.0394]	3190 [R(int) = 0.0347]
Completeness	99.90%	99.88%
Absorption correction	Gaussian	Gaussian
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	3398/0/145	3657/0/145
Goodness-of-fit on F^2	0.913	0.784
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0449,	R_1 = 0.0378,
	wR_2 = 0.1170	wR_2 = 0.1037
R indices (all data)	R_1 = 0.0492,	R_1 = 0.0470,
	wR_2 = 0.1216	wR_2 = 0.1140
Largest diff. peak and hole (eÅ^3)	4.704 and −5.509	2.21 and −2.00

1a: $[HgCl_2(Me_2SCHC(O)C_6H_4$-p-Me$)]_2$ and **2b**: $[HgBr_2(Me_2SCHC(O)C_6H_4$-p-Cl$)]_2$

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.

2.5. Sample preparation

2.5.1. Synthesis of ylides $(Me)_2SCHC(O)C_6H_4R$ (R = p-Me (a); p-Cl (b))

*$(Me)_2SCHC(O)C_6H_4$-p-Me (**a**)*: To an acetone solution (10 ml) of dimethylsulfide (0.062 g, 1.0 mmol) was added 2-bromo-4′-methylacetophenone (0.213 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 **a** [23]. IR (KBr disk): ν (cm^{-1}) 1564 (C═O) and 879 (S—C). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.32 (s, 3H, CH_3); 2.93 (s, 6H, $S(CH_3)_2$); 4.28 (1H, CH); 7.10 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.65 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.). ^{13}C NMR ($CDCl_3$, ppm): δ 20.80 (s, CH_3); 28.33 (s, $S(CH_3)_2$); 50.33 (s, CH); 125.98 (s, Ph(p)); 128.13 (s, Ph(m)); 138.08 (s, Ph(o)); 138.96 (s, Ph(i)); 182.32 (s, CO).

*$(Me)_2SCHC(O)C_6H_4$-p-Cl (**b**)*: ylide **b** was prepared following the same synthetic method as that reported for ligand **a**. Thus, dimethylsulfide (0.062 g, 1.00 mmol) was reacted with 2-bromo-4′-chloroacetophenon (0.233 g, 1.00 mmol) giving the free ligand b. IR (KBr disk): ν (cm^{-1}) 1578 (C=O) and 856 (S—C). ^{1}H NMR ($CDCl_3$): δ (ppm) 2.88 (s, 6H, $S(CH_3)_2$); 4.20 (1H, CH); 7.22 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.63 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.). ^{13}C NMR ($CDCl_3$, ppm): δ 28.09 (s, $S(CH_3)_2$); 52.46 (s, CH); 124.81 (s, Ph(*p*)); 127.35 (s, Ph(*m*)); 134.46 (s, Ph(*o*)); 139.24 (s, Ph(*i*)); 180.27 (s, CO).

2.5.2. Synthesis of complexes $[HgX_2(Me_2SCHC(O)C_6H_4$-p-Me$)]_2$ (X = Cl (**1a**), Br (**2a**), I (**3a**))

*$[HgCl_2(Me_2SCHC(O)C_6H_4$-p-Me$)]_2$ (**1a**)*: To a methanolic solution (15 ml) of $HgCl_2$ (0.135 g, 0.500 mmol) was added a methanolic solution (10 ml) of ylide **a** (0.097 g, 0.50 mmol). The mixture was stirred for 4 h. The separated solid was filtered and washed with diethyl ether [12]. Yield 0.228 g, 98%. Anal. Calc. for $Hg_2Cl_4O_2S_2C_{22}H_{28}$: C, 28.36; H, 3.03; Found: C, 28.02; H, 2.97. M.p. 192–193 °C. IR (KBr disk): ν (cm^{-1}) 1646 (CO) and 844 (S^+—C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.35 (s, 3H, CH_3); 2.92 (s, 6H, $S(CH_3)_2$); 5.49 (s, 1H, CH); 7.22 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.79 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.). ^{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).

*$[HgBr_2(Me_2SCHC(O)C_6H_4$-p-Me$)]_2$ (**2a**)*: Complex **2a** was prepared following the same synthetic method as that reported for **1a**. Thus, $HgBr_2$ (0.180 g, 0.500 mmol) was reacted with ylide **a** (0.097 g, 0.50 mmol) giving 2a [12]. Yield 0.263 g, 95%. Anal. Calc. for $Hg_2Br_4O_2S_2C_{22}H_{28}$: C, 23.82; H, 2.54; Found: C, 23.71; H, 2.49. M.p. 199–200 °C. IR (KBr disk): ν (cm^{-1}) 1637 (CO) and 825 (S^+-C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.36 (s, 3H, CH_3); 2.89 (s, 6H, $S(CH_3)_2$); 5.41 (s, 1H, CH); 7.22 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.76 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.). ^{13}C NMR (DMSO-d_6, ppm): δ 21.72 (s, CH_3); 26.89 (s, $S(CH_3)_2$); 65.46 (s, CH); 128.18 (s, Ph(*p*)); 129.46 (s, Ph(*m*)); 132.62 (s, Ph(*o*)); 144.09 (s, Ph(*i*)); 192.41 (s, CO).

*$[HgI_2(Me_2SCHC(O)C_6H_4$-p-Me$)]_2$ (**3a**)*: Complex **3a** was prepared following the same synthetic method as that reported for **1a**. Thus, HgI_2 (0.227 g, 0.500 mmol) was reacted with ylide **a** (0.097 g, 0.50 mmol) giving 3a. Yield 0.291 g, 90%. Anal. Calc. for $Hg_2I_4O_2S_2C_{22}H_{28}$: C, 20.37; H, 2.18; Found: C, 20.12; H, 2.11. M.p. 187–188 °C. IR (KBr disk): ν (cm^{-1}) 1629 (CO) and 824 (S^+-C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.35 (s, 3H, CH_3); 2.86 (s, 6H, $S(CH_3)_2$); 5.27 (s, 1H, CH); 7.21 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.74 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.). ^{13}C NMR (DMSO-d_6, ppm): δ 21.91 (s, CH_3); 27.04 (s, $S(CH_3)_2$), 65.65 (s, CH), 128.31 (s, Ph(*p*)); 129.56 (s, Ph(*m*)); 132.86 (s, Ph(*o*)); 144.189 (s, Ph(*i*)); 192.21 (s, CO).

2.5.3. Synthesis of complexes $[HgX_2(Me_2SCHC(O)C_6H_4$-p-Cl$)]_2$ (X = Cl (**1b**), Br (**2b**), I (**3b**))

*$[HgCl_2(Me_2SCHC(O)C_6H_4$-p-Cl$)]_2$ (**1b**)*: Complex **1b** was prepared following the same synthetic method as that reported for **1a**. Thus, $HgCl_2$ (0.135 g, 0.500 mmol) was reacted with ylide **b** (0.107 g, 0.50 mmol) giving 1b [12]. Yield 0.235 g, 97%. Anal. Calc. for $Hg_2Cl_6O_2S_2C_{20}H_{22}$: C, 24.70; H, 2.28; Found: C, 24.56; H, 2.23. M.p. 206–208 °C. IR (KBr disk): ν (cm^{-1}) 1647 (CO) and 824 (S^+—C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.94 (s, 6H, $S(CH_3)_2$); 5.53 (s, 1H, CH); 7.50 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.91 (d, $^3J_{HH}$ = 9.0 Hz, 2H, arom.). ^{13}C NMR (DMSO-d_6, ppm): δ 27.03 (s, $S(CH_3)_2$); 64.65 (s, CH); 129.01 (s, Ph(*m*)); 129.94 (s, Ph(*p*)); 133.82 (s, Ph(*i*)); 138.55 (s, Ph(*o*)); 191.69 (s, CO).

*$[HgBr_2(Me_2SCHC(O)C_6H_4$-p-Cl$)]_2$ (**2b**)*: Complex **2b** was prepared following the same synthetic method as that reported for **1a**. Thus, $HgBr_2$ (0.180 g, 0.500 mmol) was reacted with ylide **b** (0.107 g, 0.50 mmol) giving 2b [12]. Yield 0.264 g, 92%. Anal. Calc. for $Hg_2Br_4Cl_2O_2S_2C_{20}H_{22}$: C, 20.88; H, 1.93; Found: C, 20.55; H, 1.98. M.p. 196–198 °C. IR (KBr disk): ν (cm^{-1}) 1646 (CO) and 822 (S^+—C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.90 (s, 6H, $S(CH_3)_2$); 5.41 (s, 1H, CH); 7.49 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.86 (d, $^3J_{HH}$ = 9.0 Hz, 2H, arom.). ^{13}C NMR (DMSO-d_6, ppm): δ 27.07 (s, $S(CH_3)_2$); 65.17 (s, CH); 128.98 (s, Ph(*m*)); 129.94 (s, Ph(*p*)); 134.01 (s, Ph(*i*)); 138.49 (s, Ph(*o*)); 191.39 (s, CO).

*$[HgI_2(Me_2SCHC(O)C_6H_4$-p-Cl$)]_2$ (**3b**)*: Complex **3b** was prepared following the same synthetic method as that reported for **1a**. Thus, HgI_2 (0.227 g, 0.500 mmol) was reacted with ylide **b** (0.107 g, 0.50 mmol) giving 3b. Yield 0.287 g, 86%. Anal. Calc. for $Hg_2I_4Cl_2O_2S_2C_{20}H_{22}$: C, 17.95; H, 1.66; Found: C, 17.66; H, 1.62. M.p. 186–188 °C. IR (KBr disk): ν (cm^{-1}) 1630 (CO) and 816 (S^+—C^-). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.87 (s, 6H, $S(CH_3)_2$); 5.27 (s, 1H, CH); 7.49 (d, $^3J_{HH}$ = 8.1 Hz, 2H, arom.); 7.84 (d, $^3J_{HH}$ = 9.0 Hz, 2H, arom.). ^{13}C NMR (DMSO-d_6, ppm): δ 27.17 (s, $S(CH_3)_2$); 64.10 (s, CH); 128.94 (s, Ph(*m*)); 129.92 (s, Ph(*p*)); 134.20 (s, Ph(*i*)); 138.07 (s, Ph(*o*)); 190.07 (s, CO).

2.6. Results and discussion

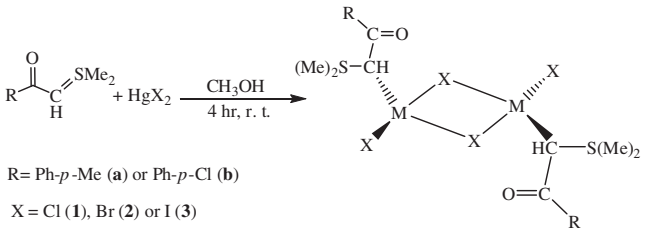
2.6.1. Synthesis

The room temperature reactions of HgX_2 (X = Cl, Br and I) with sulfonium ylides **a** and **b** (prepared by reacting dimethylsulfide with an acetone solution of 2-bromo-4′-methylacetophenone and 2-bromo-4′-chloroacetophenon and treatment with aqueous NaOH solution) for 4 h (1:1 M ratio) in CH_3OH gave the binuclear complexes **1**–**3** (a and b) (Scheme 2). Some of these complexes have been previously reported by Tewari and Awasthi [12], however only elemental analysis and infrared spectra were given, whereas herein we report comprehensive characterizations utilizing NMR spectroscopy and X-ray structural analysis. X-ray quality crystals of the complexes **1a** and **2b** were grown by the direct diffusion of methanol in the dimethylsulfoxide solution over several days.

2.6.2. Spectroscopy

In the infrared spectra the ν (CO) that is sensitive to complexation, occurs at 1564 and 1578 cm^{-1} for **a** and **b** ylides, as in the case of other resonance stabilized ylides [12]. 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 are in the range 1629–1647 cm^{-1} suggesting coordination of the ylide through carbon atom. The ν (S^+—C^-) which is also diagnostic of the coordination mode occurs at around 850 cm^{-1} in Me_2S^+—CH_2 and at about 867 cm^{-1} in ylides. In the present study, the ν (S^+—C^-) values for all complexes were shifted to lower frequencies around 820 cm^{-1}, suggesting partial removal of electron density from the S—C bond due to coordination [12].

The ^{1}H NMR signals for the SCH group of all complexes are shifted downfield compared to those of the free ylides, as a consequence of the inductive effect of the metal center [9,10]. The appearance of single signals for the SCH group in ^{1}H NMR at ambient temperature indicates the presence of only one geometrical



Scheme 2. Synthesis and reactivity of mercury(II)-sulfur ylide complexes.

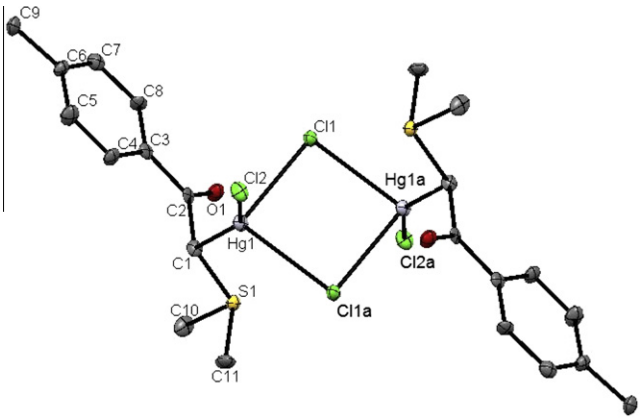


Fig. 1. ORTEP view of the X-ray crystal structure of **1a**. H atoms are omitted for clarity. Symmetry code; a: $1-x, 1-y, 2-z$.

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 [24]. The ^{13}C chemical shifts of the CO group in the complexes are around 191 ppm, relative to ~182 ppm noted for the same carbon in the parent ylides, indicating decreased shielding of this carbon atom in mercury complexes. No coupling to (^{199}Hg, 16.8% abundance, $I = 1/2$) was observed at room temperature in ^{1}H and ^{13}C NMR spectra. Failure to observe satellites in the above spectra was previously noted in the ylide complexes of Hg(II) which has been explained by fast exchange of the ylide with the metal [25].

2.6.3. Crystal structures analysis

The molecular structures of **1a** and **2b** were determined through single crystal X-ray structural analysis. The molecular drawing of complexes **1a** and **2b** are shown in Figs. 1 and 2. Crystallographic data and parameters pertaining to the data collection, structure solution and refinement are summarized in Table 1. Selected bond distances and angles, together with those of the phosphonium analogs are presented in Table 2.

The binuclear structure adopted by all complexes is in contrast to the trinuclear structure exhibited by O-coordinated of the phosphorus ylide ($Ph_3PCHCOPh$) complex of mercury(II), [26] but is similar to the structure of C-coordinated dinuclear mercury(II) halide complexes of the phosphorus ylides $Ph_3PCHC(O)OEt$ (EPPY) [27] and $Ph_3PCHC(O)Ph$ (BPPY) [28] and $Ph_3PCHC(O)C_6H_4OCH_3$ (MBPPY) [29]. The Hg(II) cenetr in complexes **1a** and **2b** is four-coordinate with sp^3 hybridization. This environment involves one short terminal Hg—X (X = Cl and Br) bond, one Hg—C bond and two asymmetric bridging Hg—X bonds.

It is generally accepted that the d orbitals of sulfur in a sulfonium group stabilize an adjacent carbanion to a greater extent than those of phosphorus in a phosphonium group [30,31]. However by comparing the sulfonium dinuclear mercury complexes with phosphorus analogs (Table 2) appears the p–d overlap of the triphenylphosphonium group to be more pronounced than that with the dimethylsulfonium groups incorporated into ylides **a** and **b**. This inversion is quite likely due to the difference in functional groups (alkyl vs. aryl) attached to the positive atom. So the dimethyl sulfonium ylides are more basic than the triphenyl phosphonium ylides, which is evident from the shorter Hg—C bond lengths in sulfonium ylides complexes compared with the equivalent distances in the phosphorus analogs (Table 2). The terminal Hg—Br bond length is very similar to that of found in phosphorus analog, although this is less true for Hg—Cl species. In contrast to the phosphorus analogs, the two bridging Hg—X bonds in **1a** are very similar. These bond lengths in **2b** are clearly asymmetric, but slightly less asymmetric than in the phosphorus analogs.

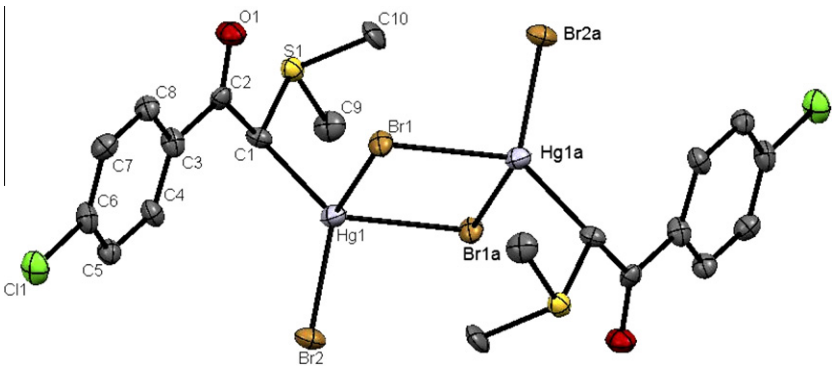


Fig. 2. ORTEP view of the X-ray crystal structure of **2b.** H atoms are omitted for clarity. Symmetry code; a: $1-x, -y, 1-z$.

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1a** and **2b** along with comparison of selected internuclear separations of them with phosphonium analogs.

Bond distance	**1a** (X = Cl)	$[Hg(MBPPY)Cl_2]_2$ [29]	**2b** (X = Br)	$[Hg(MBPPY)Br_2]_2$ [29]	Bond angles	**1a** (X = Cl)	**2b** (X = Br)
Hg1—C1	2.162(6)	2.215(4)	2.165(7)	2.218(11)	X1—Hg1—X1a	90.45	92.787(17)
Hg1—X1	2.7223(16	2.418(14)	2.6930(6	2.559(2)	S1—C1—Hg1	110.6(3)	119.8(3)
Hg1—X1a	2.7415(15)	2.884(12)	2.9596(6	2.603(3)	X2—Hg1—X	93.39(6)	94.76(2)
Hg1—X2	2.3746(17)	2.504(11)	2.5445(7)	3.022(2)	C2—C1—Hg1	107.9(4)	108.8(4)
C1—C2	1.494(9)	–	1.501(8)	–	X2—Hg1—X1	98.60(5)	102.40(2)
C1—S1	1.789(6)	–	1.801(6)	–	C1—Hg1—X2	149.77(17)	130.83(16)
C2—O1	1.231(8)	–	1.215(8)	–	C1—Hg1—X1	110.08(17)	121.88(15)
Hg···Hg	3.848	3.901	3.903	3.994	C1—Hg1—X1a	99.93(17)	102.70(16)

See Figs. 1 and 2 for the atom numbering. Symmetry code; a: $1-x, 1-y, 2-z$ (**1a**), $1-x, -y, 1-z$ (**2b**).
1a: $[HgCl_2(Me_2SCHC(O)C_6H_4\text{-p-Me})]_2$; **2b**: $[HgBr_2(Me_2SCHC(O)C_6H_4\text{-p-Cl})]_2$.

Table 3
Antibacterial activities of $[HgX_2(Me_2SCHC(O)C_6H_4\text{-}p\text{-}Me)]_2$ (X = Cl (**1a**), Br (**2a**), I (**3a**)).

	Inhibition zone (mm)								
	Concentration – 1 mg/ml			Concentration – 0.1 mg/ml			Concentration – 0.01 mg/ml		
Microorganism	**1a**	**2a**	**3a**	**1a**	**2a**	**3a**	**1a**	**2a**	**3a**
P. vulgaris (−)	17 ± 0.18[a]	16 ± 0.25[a]	17 ± 0.56[a]	10 ± 0.24[b]	10 ± 0.16[b]	11 ± 0.36[b]	Na	7 ± 0.26[c]	9 ± 0.12[c]
E. coli (−)	21 ± 0.34[a]	20 ± 0.33[a]	20 ± 0.44[a]	15 ± 0.46[b]	10 ± 0.14[b]	10 ± 0.28[b]	13 ± 0.28[c]	7 ± 0.14[c]	7 ± 0.00[c]
B. cereus (+)	15 ± 0.26[a]	22 ± 0.33[a]	22 ± 0.66[a]	10 ± 0.26[b]	10 ± 0.11[b]	14 ± 0.18[b]	Na	7 ± 0.00[c]	8 ± 0.22[c]
S. aureus (+)	25 ± 0.66[a]	22 ± 0.43[a]	25 ± 0.48[a]	10 ± 0.15[b]	10 ± 0.22[b]	13 ± 0.15[b]	7 ± 0.15[c]	8 ± 0.00[c]	Na
B. megaterium (+)	22 ± 0.54[a]	20 ± 0.38[a]	21 ± 0.25[a]	16 ± 0.36[b]	10 ± 0.33[b]	10 ± 0.34[b]	7 ± 0.00[c]	8 ± 0.18[c]	7 ± 0.14[c]
S. marcescens (−)	14 ± 0.15[a]	14 ± 0.22[a]	12 ± 016[a]	10 ± 0.22[b]	10 ± 0.14[b]	9 ± 0.15[b]	8 ± 0.24[c]	7 ± 0.14[c]	8 ± 0.16[c]

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for any bacteria in different concentrations) are significantly different ($P < 0.05$).
Na: No active.

Table 4
Antibacterial activities of $[HgX_2(Me_2SCHC(O)C_6H_4\text{-}p\text{-}Cl)]_2$ (X = Cl (**1b**), Br (**2b**), I (**3b**)).

	Inhibition zone (mm)								
	Concentration – 1 mg/ml			Concentration – 0.1 mg/ml			Concentration – 0.01 mg/ml		
Microorganism	**1b**	**2b**	**3b**	**1b**	**2b**	**3b**	**1b**	**2b**	**3b**
P. vulgaris (−)	14 ± 0.18[a]	16 ± 0.34[a]	17 ± 0.16[a]	12 ± 0.14[b]	10 ± 0.26[b]	10 ± 0.24[b]	Na	7 ± 0.15[c]	7 ± 0.00[c]
E. coli (−)	17 ± 0.14[a]	16 ± 0.26[a]	32 ± 0.66[a]	14 ± 0.28[b]	9 ± 0.22[b]	20 ± 0.33[b]	Na	7 ± 0.00[c]	10 ± 0.14[c]
B. cereus (+)	20 ± 0.35[a]	20 ± 0.18[a]	18 ± 0.24[a]	14 ± 0.33[b]	8 ± 0.17[b]	11 ± 0.15[b]	9 ± 0.33[c]	Na	Na
S. aureus (+)	22 ± 0.54[a]	14 ± 0.22[a]	17 ± 0.14[a]	18 ± 0.25[b]	10 ± 0.15[b]	Na	12 ± 0.25[c]	7 ± 0.14[c]	Na
B. megaterium (+)	25 ± 0.64[a]	12 ± 0.18[a]	15 ± 0.14[a]	15 ± 0.12[b]	Na	11 ± 0.18[b]	11 ± 0.17[c]	Na	7 ± 0.11[c]
S. marcescens (−)	10 ± 0.14[a]	14 ± 0.24[a]	12 ± 0.18[a]	8 ± 0.00[b]	11 ± 0.18[b]	8 ± 0.00[b]	Na	7 ± 0.00[c]	Na

Experiment was performed in triplicate and expressed as mean ± SD. Values with different superscripts within each column (for any bacteria in different concentrations) are significantly different ($P < 0.05$).
Na: No active.

Table 5
Antibacterial activity of antibiotics as positive controls and DMSO solve as negative control.

	Inhibition zone (mm)				
	Positive controls				Negative controls
Microorganism	Gentamicin	Penicillin	Nitrofurantoin	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: No active.

The angles subtended by the ligands at the Hg(II) center vary from 90.45(4)° to 149.77(17)° in **1a** and 92.787(17)° to 130.83(16)° in **2b**, indicating very distorted tetrahedral coordination geometry. The widening of the X—Hg—C angle from the tetrahedral angle must be due to the higher s character of the sp^3 hybrid mercury orbitals involved in the above bonds and the formation of a strong halide-bridge between Hg atoms which requires the internal X—Hg—X angles 90.45(4)° **1a** and 92.787(17)° **2b** to be considerably smaller. The two mercury atoms and two bridging halides in each case are perfectly coplanar. The internuclear distances between mercury atoms at the distances of 3.848 **1a** and 3.903 Å **2b** are less than in the phosphonium analogs (Table 2), but these distances are much longer than the sum of Van der Waals radii (3.0 Å) of the two mercury atoms [32] indicating the absence of significant bonding interactions between the mercury atoms in the molecular structures. The adaptation of binuclear structures in Hg(II) ylide complexes may be explained both by the preference of Hg(II) for four coordination and the stability of the 18 electron configuration around Hg(II).

2.6.4. Antibacterial activity

Results from antibacterial assessments of the samples are presented in Tables 3 and 4. Positive controls and negative control are in Table 5. All complexes display antibacterial activity against the bacteria tested especially for the Gram positive ones. In contrast, *Serratia marcescens* (−) was the most resistant bacterium. With comparing their antibacterial activities with those of reference antibiotics, it seems that the complexes have remarkable inhibitory potencies against bacteria. Generally the antibacterial activity of compounds is attributed mainly to its major components. However, today it is known that the synergistic or antagonistic effect of one compound even when it is a minor component of mixture has to be considered. The complexes reported herein showed more activity against some bacteria, than others, under identical experimental conditions. This would suggest that the structure of complexes may reduce the polarity of the metal ion mainly. Also, we can consider that the formation of a neutral coordination complex may facilitate crossing of the lipid layer of the bacterial cell membrane and in this way may be effected the mechanisms of growth

and development of bacteria. Composition of the coordination site and the geometry of the tested complexes seemed to be the principal factor that influences the antibacterial activity. The presence of H, Br, Cl and I groups exerts a number of changes on antibacterial activity of the tested complexes (Tables 3 and 4). The above results indicate that the complexes studied may be used in the treatment of diseases caused by the bacteria that were tested. Further studies are needed to evaluate the *in vivo* potential of these compounds in animal models.

3. Concluding remarks

The present study describes the synthesis and characterization of some binuclear mercury(II) complexes of sulfonium ylides. On the basis of the physico-chemical and spectroscopic data is clear that the sulfonium ylide ligands exhibit monodentate C-coordination to the metal centers. The mercury complexes of sulfonium ylides reported herein are structurally characterized for the first time. The single crystal X-ray analysis reveals the presence of an asymmetric halide-bridge binuclear structure for these complexes similar to that observed for phosphonium ylide analogs. A comparison of important bond lengths and angles reveals a significant difference between the Hg—C bond lengths that is attributed to Lewis basicity of dialkylsulfonium ylides ligands vs. triarylphosphonium ylide ligands. Results from the present study clearly demonstrate that the complexes exhibit significant antibacterial activity, which may help to inform the design of improved antibacterial agents.

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Appendix A. Supplementary material

CCDC-865651 and 865652 contain the supplementary crystallographic data for complexes **1a** and **2b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.10.051.

References

[1] J. Stephen Clark, Nitrogen, Oxygen and Sulfur Ylide Chemistry, A Practical Approach in Chemistry, Oxford University Press, Britain, 2002.
[2] V.K. Aggarwal, J.L. Vasse, Org. Lett. 5 (2003) 3987.
[3] S. Deuerlein, D. Leusser, U. Flierler, H. Ott, D. Stalke, Organometallics 27 (2008) 2306.
[4] M. Gandelman, K.M. Naing, B. Rybtchinski, E. Poverenov, Y. Ben-David, N. Ashkenazi, R.M. Gauvin, D. Milstein, J. Am. Chem. Soc. 127 (2005) 15265.
[5] E. Serrano, T. Soler, R. Navarro, Esteban P. Urriolabeitia, J. Mol. Struct. 890 (2008) 57.
[6] L. Weber, Angew. Chem. Int. Ed. Engl. 22 (1983) 516.
[7] I. Kawafune, G. Matsubayashi, Inorg. Chim. Acta 70 (1983) 1.
[8] G. Matsubayashi, I. Kawafune, T. Tanaka, S. Nishigaki, K. Nakatsu, J. Organomet. Chem. 187 (1980) 113.
[9] S.J. Sabounchei, A. Dadrass, M. Jafarzadeh, S. Salehzadeh, H.R. Khavasi, J. Organomet. Chem. 692 (2007) 2500.
[10] S.J. Sabounchei, H. Nemattalab, S. Salehzadeh, M. Bayat, H.R. Khavasi, H. Adams, J. Organomet. Chem. 2008 (1975) 693.
[11] E.T. WeleskiJr, J.L. Silver, M.D. Jansson, J.L. Burmeister, J. Organomet. Chem. 102 (1975) 365.
[12] R.S. Tewari, A.K. Awasthi, J. Organomet. Chem. 271 (1984) 403.
[13] B. Li, S. Yu, J.Y. Hwang, S. Shi, J. Miner, Mater. Charact. Eng. 1 (2002) 61.
[14] P.M. Bennett, Br. J. Pharmacol. 153 (2008) S347.
[15] G.D. Wright, Adv. Drug Deliver. Rev. 57 (2005) 1451.
[16] S. Gibbons, Phytochem. Rev. 4 (2005) 63.
[17] T.E. Renau, S.J. Hecker, V.J. Lee, Ann. Rep. Med. Chem. 33 (1998) 121.
[18] G.D. Wright, Chem. Biol. 7 (2000) R127.
[19] CrysAlisPro, Agilent Technologies, Version 1.171.35.19 (release 27-10-2011 CrysAlis171.NET) (compiled October 27 2011,15:02:11).
[20] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[21] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Cryst. 42 (2009) 339.
[22] O.A. Awoyinka, I.O. Balogun, A.A. Ogunnowo, J. Med. Plants Res. 3 (2007) 63.
[23] K.W. Ratts, A.N. Yao, J. Org. Chem. 31 (1966) 1185.
[24] J.A. Albanese, D.L. Staley, A.L. Rheingold, J.L. Burmeister, Inorg. Chem. 29 (1990) 2209.
[25] N.L. Holy, N.C. Baenziger, R.M. Flynn, D.C. Swenson, J. Am. Chem. Soc. 98 (1976) 7823.
[26] B. Kalyanasundari, K. Panchanatheswaran, V. Parthasarathi, W.T. Robinson, Bull. Chem. Soc. Jpn. 72 (1999) 33.
[27] E.C. Spencer, M.B. Mariyatra, J.A.K. Howard, A.M. Kenwright, J. Organomet. Chem. 692 (2007) 1081.
[28] M. Kalyanasundari, K. Panchanatheswaran, W.T. Robinson, H. Wen, J. Organomet. Chem. 491 (1995) 103.
[29] S.J. Sabounchei, V. Jodaian, H.R. Khavasi, Polyhedron 26 (2007) 2845.
[30] A.W. Johnson, R.B. LaCount, Tetrahedron 9 (1960) 130.
[31] W.von E. Doering, A.K. Hoffmann, J. Am. Chem. Soc. 77 (1955) 621.
[32] J.E. Huheey, Inorganic Chemistry Principles of Structure and Reactivity, 2nd ed., Harper and Row, New York, 1978.