NJC

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c3nj00729d

Synthesis, crystal structure investigation, DFT analyses and antimicrobial studies of silver(I) complexes with *N,N,N′,N″*-tetrakis(2-hydroxyethyl/propyl) ethylenediamine and tris(2-hydroxyethyl)amine†

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Received (in Montpellier, France) 3rd July 2013, Accepted 29th November 2013

DOI: 10.1039/c3nj00729d

www.rsc.org/njc

The synthesis, crystal structures, DFT and antimicrobial studies of three novel complexes of silver: $[Ag(THEEN)]_2(PIC)_2$ (**1**), $[Ag(THPEN)]_2(PIC)_2$ (**2**) and $[Ag(TEAH_3)_2](PIC)$ (**3**), have been reported in the present work, where THEEN/THPEN (*N,N,N′,N″*-tetrakis(2-hydroxyethyl/propyl)ethylenediamine) are tetrapodal ligands and $TEAH_3$ (tris(2-hydroxyethyl)amine) is a tripodal ligand. Complexes (**1**) and (**2**) are dinuclear, whereas (**3**) is mononuclear. Complex (**1**) adopted a see-saw geometry with coordination number four, whereas (**2**) and (**3**) are five coordinated. Complex (**2**) acquired distorted square-pyramidal geometry, whereas complex (**3**) acquired distorted trigonal-bipyramidal geometry. Extensive hydrogen bonding interactions have been found in all three complexes. The primary coordination sphere of the newly synthesized silver(I) complexes has been optimized, structural parameters have been calculated and the energy gaps of the frontier orbitals have been predicted with the B3LYP/6-31G/LANL2DZ level of theory. Structural parameters from the crystallographic and DFT studies are in good agreement with each other. The relatively smaller calculated HOMO–LUMO energy gaps (HLG) suggest charge transfer transitions. Antimicrobial studies have been performed with the new silver(I) complexes against gram +ve bacteria (*Staphylococcus aureus*), gram −ve bacteria (*Serratia marcescens*, *Sphingobium japonicum* and *Stenotrophomonas maltophilia*) and fungal species (*Candida albicans*, *Aspergillus niger* and *Saccharomyces cerevisiae*). Dinuclear complexes (**1**) and (**2**) exhibited remarkable results. All the synthesized silver(I) complexes have been proven to be better antibacterial and antifungal agents, even than their standard drugs (ciprofloxacin and fluconazole) and can be used as effective antimicrobial agents and potential drugs in the future.

1 Introduction

A unique feature of the coordination chemistry of silver(I) is its ability to form complexes with a variety of ligands that have all types of donor atoms resulting in the formation of supramolecular compounds.[1] Silver(I) complexes with monocarboxylic acid antibiotics monensin, lasalocid, and D-lactobionate have been reported.[2–5] Silver(I) compounds with N-donor ligands adopt novel structures, such as multi dimensional helical, honeycomb channel, interwoven diamondoid, graphite framework *etc.* The construction of oligopyridines and oligophenanthroline with Ag(I) generally results in the formation of single, double or triple standard helicates.[6–13] The coordination chemistry of silver(I) with aromatic ligands has extended π-systems and also leads to the formation of supramolecular structures having π–π interactions.[14–16] Hydrogen bonding interactions are also responsible for supramolecular interactions, as are formed in amide moieties having infinite chains through N–H···O interactions belonging to some silver complexes.[17,18] The supramolecular structure has both π–π and H-bonding interactions in $\{1,2,4,5\text{-}C_6H_2[CH_2OCH_2C(pz)_3]_4\ Ag_2(BF_4)_2\}_n$.[19]

Silver(I) has a relatively low affinity for oxygen atoms, although a few complexes with β-diketonates, carboxylates and crown ethers are well known.[1] The complex formation of noncyclic polyethers, crown ethers and large crown ethers have been reported.[20,21] The most frequently used crown ether is the dibenzo-18-crown-6-ether for which silver(I) prefers an octahedral coordination and forms close dinuclear complexes based on cation–π interactions in an η^2 fashion.[22]

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† Electronic supplementary information (ESI) available. CCDC 919841, 936204 and 929555. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00729d

Silver(I) complexes not only have a beautiful architecture, but also possess useful applications. For instance, β-diketonates derivatives of silver(I) can be easily converted into metallic silver by metal organic chemical vapour deposition (MOVCD) thermal decomposition techniques.[23] The complexes of silver(I) with polyether tetraglymes are useful in the fabrication of silver-based films.[24]

Silver and its complexes are known for their effective antibacterial, antifungal,[25–32] antiseptic,[33] anti-inflammatory[34] and antitumour[35,36] activities. The antimicrobial properties of silver(I) complexes depend upon the nature of the atoms coordinated to the silver ion and its bonding properties, rather than the solubility, charge, chirality or degree of polymerization.[37] The coordinating ligands of the silver(I) complexes play the role of carrier for the silver(I) ions to the biological system.[38] In silver(I) complexes, Ag–O and Ag–N bond strengths also play an important role in exhibiting a wider spectrum of antimicrobial and antifungal activities and are the potential target sites for the inhibition of bacterial and yeast growth.[37,38] Ag(I)–S complexes[39] possess a narrower spectrum of antibacterial activity than silver(I)–N[26,28] and silver(I)–O complexes,[27,29,38,40] whereas silver(I)–P[41] based coordination complexes have shown no activity against bacterial strains, yeast and molds. The effective antimicrobial activities of Ag(I)–N and Ag(I)–O bonded complexes are due to the weak silver(I)–N and silver(I)–O bonds and can be easily replaced with biomolecules, especially with those of thiol groups.[37] The antimicrobial activities of silver(I)–O complexes support the fact that the coordination geometry around the silver(I) influences the strength of antimicrobial activities and also the ligand – exchangeability of the silver(I) complexes plays a significant role in the magnitude of antimicrobial activities. Many water soluble and light sensitive silver(I) complexes with amino acids[26,28,37] and with chiral and racemic camphanic acid show potential antimicrobial activity against a number of bacterial strains. Silver(I) complexes containing various types of ligands, such as carboxylic acids,[42] amino acids,[43] nitrogen,[44] phosphorus or sulphur[45] donor ligands also exhibit selectivity against a variety of cancer cells. The present work describes the synthesis, crystal structures, DFT analyses and antimicrobial activities of three novel silver(I) complexes: $[Ag(THEEN)]_2(PIC)_2$ (**1**), $[Ag(THPEN)]_2(PIC)_2$ (**2**) and $[Ag(TEAH_3)_2](PIC)$ (**3**). Previously the complex of silver(I) ion with ligand THEEN has been studied under the influence of sacchrinate anion.[46a]

2 Results and discussion

2.1 Description of crystal structures (1), (2) and (3)

The crystal data and the refinement details of the silver(I) complexes are given in Table 1. Selected bond distances, bond angles and hydrogen bonding geometry interactions are listed in Tables 2 and 3 respectively.

2.1.1 $[Ag(THEEN)]_2(PIC)_2$ (1). The molecular structure of the dinuclear silver complex (**1**) contains two Ag(I) ions, two tetrapodal ligands (THEEN) with polar hydroxyl groups and two picrate anions (Fig. 1a). Each silver(I) ion has coordination number four and see-saw geometry (Fig. 1b) is proposed for it

Table 1 Crystal data and structure refinement for complexes (**1**), (**2**) and (**3**)

Complexes	$[Ag(THEEN)]_2(PIC)_2$ (**1**)	$[Ag(THPEN)]_2(PIC)_2$ (**2**)	$[Ag(TEAH_3)_2](PIC)$ (**3**)
Empirical formula	$C_{32}H_{52}Ag_2N_{10}O_{22}$	$C_{40}H_{68}Ag_2N_{10}O_{22}$	$C_{18}H_{32}AgN_5O_{13}$
Formula weight	1144.58	1256.78	634.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal size	0.13 × 0.10 × 0.09	0.14 × 0.10 × 0.08	0.13 × 0.11 × 0.09
Color	Yellow	Yellow	Yellow
Shape	Prism	Needle	Needle
Space group	$P21/c$	$P21/n$	$P21/c$
Unit cell dimensions (Å), (°)	$a = 8.886(14)$, $\alpha = 90$	$a = 12.796(10)$, $\alpha = 90$	$a = 9.194(5)$, $\alpha = 90$
	$b = 19.167(3)$, $\beta = 91.75(5)$	$b = 15.621(2)$, $\beta = 94.29(2)$	$b = 20.9520(5)$, $\beta = 108.31(5)$
	$c = 13.127(2)$, $\gamma = 90$	$c = 13.283(3)$, $\gamma = 90$	$c = 13.625(5)$, $\gamma = 90$
Volume (Å^3), Z	2234.7(6), 2	2647.6(7), 2	2491.7(17), 4
$\rho_{calc.}$ g cm^{-3}	1.701	1.577	1.691
μ (cm^{-1})	0.969	0.826	0.884
$F_{(000)}$	1168.0	1296	1304.0
T (K)	296(2)	296(2)	296(2)
θ Range of data collection	1.88 to 32.78	2.02 to 26.51	1.85 to 24.83
Limiting frequency	$-13 \leq h \leq 13$	$-16 \leq h \leq 16$	$-10 \leq h \leq 10$
	$-28 \leq k \leq 28$	$-13 \leq k \leq 19$	$-24 \leq k \leq 24$
	$-19 \leq l \leq 19$	$-16 \leq l \leq 16$	$-15 \leq l \leq 15$
Total reflections	24 944	21 660	29 302
Independent reflections	7859 [R(int) = 0.0409]	5477 [R(int) = 0.0248]	4245 [R(int) = 0.0828]
Data/restraints/parameters	7859/4/310	5477/5/351	4245/12/352
Completeness to $\theta = 25.00$	95.0%	99.7%	98.7%
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2	Full matrix least squares on F^2
Goodness of fit on F^2	1.150	1.012	1.089
Final R indices [$I > 2(I)$]	$R_1 = 0.0769$, w$R_2 = 0.1553$	$R_1 = 0.0347$, w$R_2 = 0.0828$	$R_1 = 0.0422$, w$R_2 = 0.0985$
R indices (all data)	$R_1 = 0.1245$, w$R_2 = 0.1786$	$R_1 = 0.0449$, w$R_2 = 0.0881$	$R_1 = 0.0671$, w$R_2 = 0.1145$
Largest diff. peak & hole (e Å^3)	2.298 and −1.288	0.600 and −0.387	0.849 and −0.408
CCDC no.	919841	936204	929555

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

Bond lengths		Bond angles	
Complex (**1**)			
Ag–N1	2.452 (4)	N1–Ag–N2	78.56 (14)
Ag–N2	2.438 (4)	N1–Ag–O1	71.20 (14)
Ag–O1	2.595 (5)	N1–Ag–O4B	134.27 (14)
Ag–O4B	2.386 (4)	N2–Ag–O4B	144.09 (14)
Ag· · ·AgB	3.236 (9)	N2–Ag–O1	125.35 (13)
		O4B–Ag–O1	85.30 (14)
Complex (**2**)			
Ag–N1	2.479 (2)	N1–Ag–N2	78.03 (9)
Ag–N2	2.437 (2)	N1–Ag–O1	69.70 (9)
Ag–O1	2.558 (3)	N1–Ag–O3B	137.26 (8)
Ag–O3B	2.471 (2)	N2–Ag–O3B	141.33 (7)
Ag–O4	2.639 (2)	N2–Ag–O1	127.92 (8)
Ag· · ·AgB	3.233 (5)	N2–Ag–O4	69.61 (8)
		O3B–Ag–O1	82.52 (7)
		O1–Ag–O4	161.12 (8)
		O4–Ag–N1	125.97 (8)
Complex (**3**)			
Ag–N1	2.346 (4)	N1–Ag–O1	72.94 (12)
Ag–N2	2.276 (3)	N1–Ag–O2	71.30 (15)
Ag–O1	2.675 (4)	N1–Ag–O3	73.99 (12)
Ag–O2	2.717 (5)	N2–Ag–N1	174.46 (12)
Ag–O3	2.660 (4)	N2–Ag–O3	106.38 (12)
		N2–Ag–O2	103.43 (14)
		O1–Ag–O2	107.42 (13)
		O1–Ag–O3	121.63 (11)
		O1–Ag–N2	110.87 (12)
		O2–Ag–O3	105.55 (13)

Symmetry transformations used to generate equivalent atoms: [Symmetry code complex (**1**) $B = 2 - x, 1 - y, 2 - z$: complex (**2**) $B = 2 - x, 1 - y, 2 - z$].

Table 3 Selected H-bond interactions (Å, °) for complexes (**1**), (**2**) and (**3**)

Hydrogen bonding geometry				
D–H· · ·A	d(D–H)	d(H–A)	d(D–A)	∠(DHA)
Complex (**1**)				
O1–H1· · ·O3B	0.83 (5)	1.99 (5)	2.78 (6)	158 (5)
O3–H3· · ·O5A	0.84 (4)	2.13 (5)	2.81 (6)	137 (3)
O3–H3· · ·O6A	0.84 (4)	2.32 (5)	2.97 (7)	134 (4)
Complex (**2**)				
O1–H1· · ·O4B	0.81 (2)	1.94 (2)	2.76 (3)	176 (2)
O4–H4· · ·O5A	0.79 (3)	2.00 (3)	2.71 (3)	149 (3)
O4–H4· · ·O11A	0.79 (3)	2.40 (4)	3.00 (4)	133 (3)
Complex (**3**)				
O1–H1· · ·O7B	0.83 (3)	1.94 (3)	2.76 (4)	170 (4)
O3–H3· · ·O4B	0.82 (2)	2.03 (2)	2.83 (5)	167 (2)
O4–H4· · ·O5C	0.83 (3)	1.89 (3)	2.68 (5)	157 (2)
O5–H5· · ·O7B	0.81 (5)	2.00 (5)	2.77 (5)	158 (4)
O5–H5· · ·O13B	0.81 (5)	2.34 (4)	2.90 (6)	127 (3)
O6–H6· · ·O1A	0.84 (4)	1.99 (3)	2.78 (5)	156 (3)

Complex (**1**): $A = x, 1/2 - y, 1/2 + z$, $B = 2 - x, 1 - y, 2{-}z$; complex (**2**): $A = 1 - x + 1/2, y - 1/2, 1 - z + 1/2$, $B = 2 - x, 1 - y, 2 - z$: complex (**3**): $A = -x, -y, 2 - z$, $B = x, 1/2 - y, z + 1/2$, $c = x, 1/2 - y, -1/2 + z$.

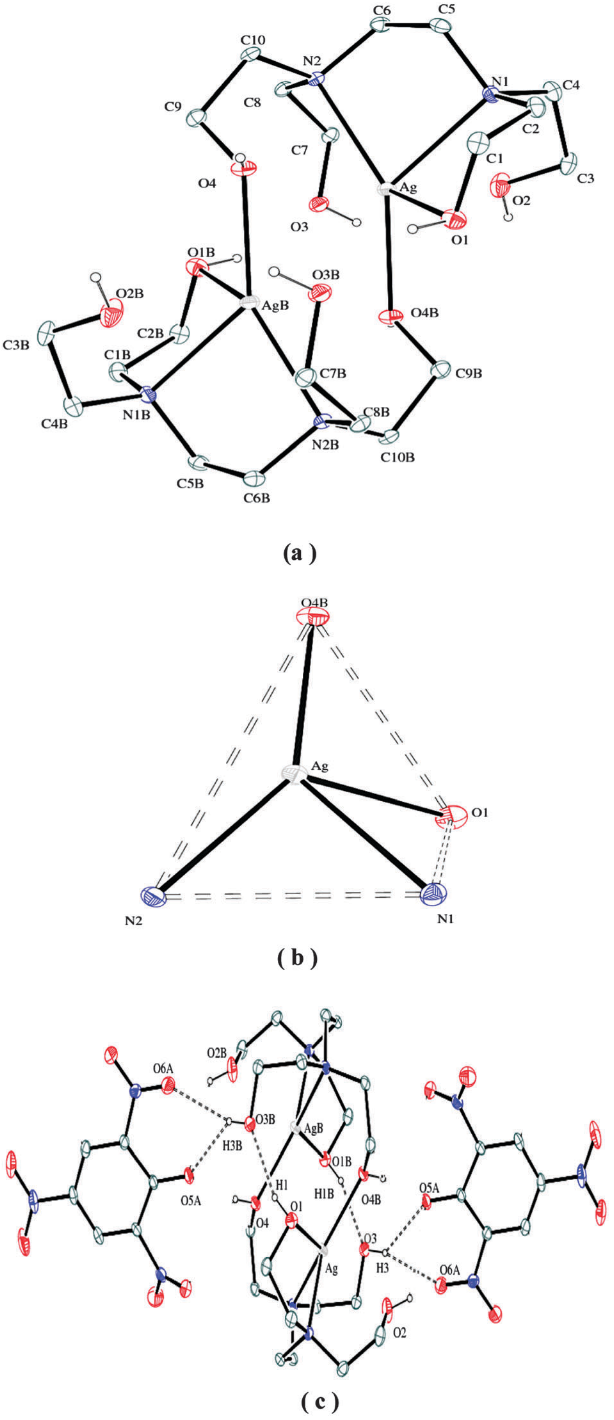
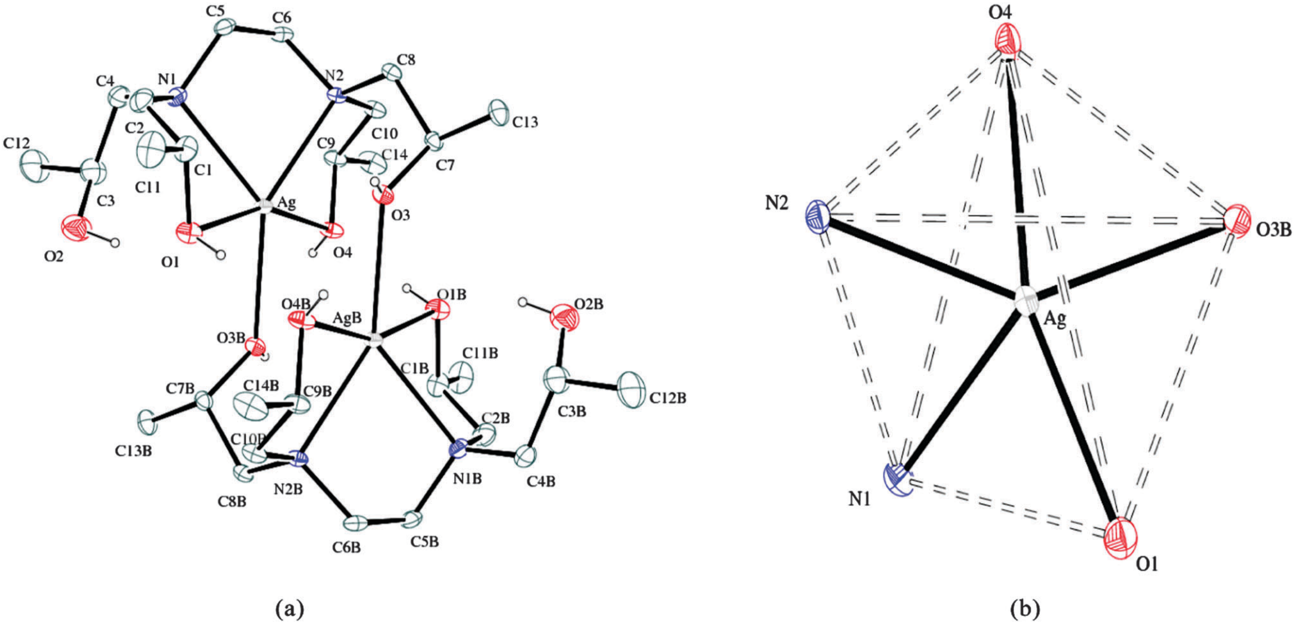


Fig. 1 (a) ORTEP diagram of $[Ag(THEEN)]_2(PIC)_2$ complex with atom labelling scheme. Picrate anions and hydrogen attached to the carbon atoms have been omitted for clarity. [Symmetry code: $B = 2 - x, 1 - y, 2 - z$] (b) see-saw geometry of the complex. (c) Molecular structure of the complex with hydrogen bonding interactions [Symmetry code: $A = x, 1/2 - y, 1/2 + z$, $B = 2 - x, 1 - y, 2 - z$].

on the basis of the simple geometry index tau (τ = 0.62) for a four coordinate complex.[46b] See-saw geometry has been reported in the literature for some of the silver and copper complexes.[46] In complex (**1**), each THEEN ligand is coordinated to the silver ion through its two amine nitrogens and one hydroxyl oxygen O1. The fourth coordination site around each silver(I) ion is occupied by hydroxyl oxygens from another THEEN ligand present in the unit cell. The other two hydroxyl oxygens of each ligand are non-coordinating and are involved only in hydrogen bonding interactions. The fourth hydroxyl oxygen of each THEEN ligand asymmetrically bridges between the two Ag$^+$ ions. The picrate anions do not directly interact with the metal ion but remain outside the coordination sphere in the present complex. There are intermolecular hydrogen bonding interactions between the donor polar hydroxyl groups of tetrapodal THEEN and acceptor picrate anions through oxygens of the phenolic and the nitro groups in the crystal structure (Fig. 1c) (Table 3). The hydroxyl oxygen O3 is extensively involved in hydrogen bonding interactions as it is non-coordinated. The oxygen also acts as a double donor of hydrogen bonds to the oxygen atoms O5 and O6 belonging to the phenolate and nitro group of the picrate anion respectively, as well as an acceptor of hydrogen bonds from the hydroxyl oxygen of the neighbouring molecule. Overall, the picrate anions join together several binuclear units of [Ag(THEEN)]$_2$ (Fig. S1, ESI†) resulting in the formation of a zig-zag polymer chain. Fig. S2 (ESI†) shows a top view of the zig-zag polymer chain of complex [Ag(THEEN)]$_2$(PIC)$_2$, extended along the crystallographic '*c*' axis.

2.1.2 [Ag(THPEN)]$_2$(PIC)$_2$ (2). An ORTEP representation of the structure, including the atomic numbering scheme is given in Fig. 2a. The molecular structure of the dinuclear complex (**2**) consists of two silver(I) ions, two tetrapodal ligands (THPEN) and two picrate anions. Each silver(I) ion is coordinated through two nitrogen and two oxygen atoms of one THPEN ligand and a third oxygen atom belonging to another THPEN ligand of the dinuclear unit (Fig. 2a). The geometry around each silver ion can be described as distorted square-pyramidal based on the angular structural parameter (τ = 0.33) for five coordinate molecules.[46c] O4 is the axial donor atom lying above the plane and is tetragonally elongated, whereas the N1, N2, O1 and O3B donor atoms of the THPEN ligand are in equatorial positions forming one plane (Fig. 2b). The hydroxyl oxygens O3 and O3B belonging to both the THPEN ligands bridge between two silver(I) centres. The hydroxyl oxygens O2 and O2B of each THPEN ligand are non-coordinating and are involved only in the hydrogen bonding interactions. The picrate anions do not directly interact with the metal ions but remain outside the coordination sphere in the title complex. There are intermolecular hydrogen bonding interactions involving the hydroxyl, phenolic and oxygens of the nitro groups of the picrate anions in the crystal structure (Fig. S3, ESI†). The polar hydroxyl groups of the tetrapodal ligand (THPEN) act as H-bond donors towards the acceptor picrate anions through phenolic and nitro oxygens (Table 3). The hydroxyl oxygen O4 is extensively involved in hydrogen bonding interactions as it is non-coordinated.

The hydroxyl oxygen O4 acts as a double donor of hydrogen bonds to the oxygen atoms O5 and O11 belonging to the phenolate and nitro group of the picrate anion respectively, as well as an acceptor of hydrogen bonds from the hydroxyl oxygen of the neighbouring molecule (Fig. S3, ESI†). Overall, the picrate anions join together several binuclear units of [Ag(THPEN)]$_2$ (Fig. S4, ESI†) resulting in the formation of a zig-zag polymer chain. Fig. S5 (ESI†) shows a top view of zig-zag polymer chain of complex [Ag(THPEN)]$_2$(PIC)$_2$, extended along the crystallographic '*c*' axis. The distance between two Ag···Ag in complexes (**1**) and (**2**) are 3.236 Å and 3.233 Å, which are longer than the Ag–Ag separation in metallic silver (2.88 Å)[47] and indicate the existence of van der Waals contact between these two silver(I) ions. This Ag–Ag distance is longer than $\{[\mathrm{Ag(othf)}]_2\}_n$ (2.781(1) to 2.823(2) Å and $\{[\mathrm{Ag(hpyrrld)}]_2\}_n$ (2.875(2)–2.9022(7) Å),[48] $\{[\mathrm{Ag_2(S\text{-}ca)_2}]\}_n$, 3.0963 (11) and $\{[\mathrm{Ag_2(ca)_2(Hca)_2}]\}_n$, 3.1087(7) but smaller than earlier reported



(a) (b)

Fig. 2 (a) ORTEP diagram of [Ag(THPEN)]$_2$(PIC)$_2$ complex with atom labelling scheme. Picrate anions and hydrogen attached to the carbon atoms have been omitted for clarity. [Symmetry code: *B* = 2 − *x*, 1 − *y*, 2 − *z*] (b) distorted square-pyramidal view of the complex.

in {[Ag_2(R-ca)$_2$(R-Hca)$_2$]}$_n$ 3.4167(6) and {[Ag_2(S-ca)$_2$(S-Hca)$_2$]}$_n$, 3.44025(14)[41] complexes. The number of dinuclear Ag(I) complexes [Ag_2(sac)$_2$(pen)$_2$],[49] [Ag_2(sac)$_2$(pyet)$_2$],[50] [Ag(sac)(mpr)]$_2$,[51] [Ag_2(sac)$_2$(dmen)$_2$],[52] [Ag_2(sac)$_2$(μ-aepy)$_2$][53] with different ligands in the presence of saccharinate anion has been reported earlier.

Complexes (**1**) and (**2**) are of a charge-separated nature as the counter anions, picrates are present outside the coordination sphere of both silver ions, whereas in the earlier reported complex of silver saccharinate with tetrapodal THEEN has an ion-paired nature, as the counter anion saccharinate directly interacts with silver(I) ion.[46a]

2.1.3 [Ag($TEAH_3$)$_2$] (PIC) (3). [Ag($TEAH_3$)$_2$] (PIC) (**3**) is a mononuclear complex. The molecular structure consists of one silver ion, two triethanolamine ($TEAH_3$) ligands and one picrate anion (Fig. 3a). One of the tripodal ligand acts as tetradentate, while another acts as a monodentate ligand. This mode of coordination of the $TEAH_3$ ligand is unique and is found only in the present complex, although a number of complexes of $TEAH_3$ with different modes of coordination with some s-block,[54–56] d-block[57,58] metal ions and lanthanoids[59] have been structurally characterized and reported.

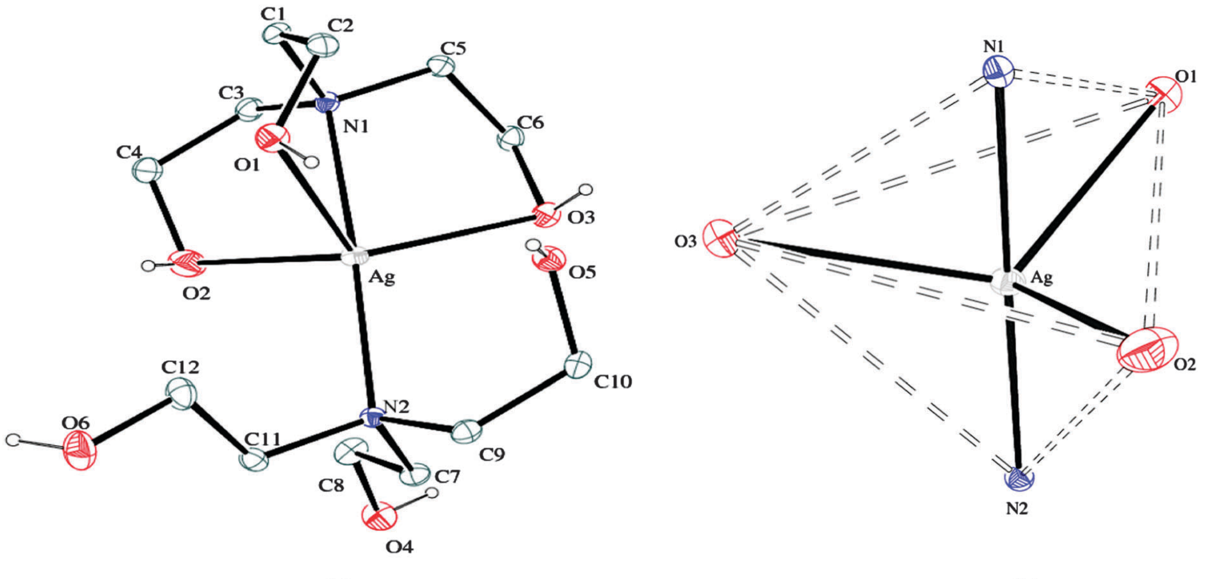
The coordination number of the silver ion in complex (**3**) is five and it has a distorted trigonal-bipyramidal geometry (Fig. 3b). The geometry around the five coordinate silver ion can be described as distorted trigonal-bipyramidal according to Addison's approach[46c] of angular structural parameter (τ = 0.88). O3, N2 and O1 donor atoms of the $TEAH_3$ ligand define the trigonal plane and occupy the equatorial positions, whereas the axial positions are occupied by N1 and N2. The bond angle of N1–Ag–N2 is 174.46(12)°. The nature of [Ag($TEAH_3$)$_2$] (PIC) (**3**) is charge–separated as the picrate anion is present outside the coordination sphere and interacts indirectly by coordinating through its amine nitrogen and all three hydroxyl oxygen atoms. All the polar hydroxyl groups of the tripodal ligand ($TEAH_3$) and oxygens of phenolic, as well as nitro groups belonging to the picrate anion, are involved in hydrogen bonding interactions in complex (**3**). The tripodal ligand donates hydrogen bonds through its polar hydroxyl groups, whereas the picrate accepts hydrogen bonds through its oxygen. The non-coordinated hydroxyl oxygen O5 of monocoordinated $TEAH_3$ is more extensively involved in hydrogen bonding interactions rather than other hydroxyl oxygens and acts as a double donor, as well as an acceptor of hydrogen bonds (Fig. S6, ESI†). Picrate anions join together several mononuclear units of [Ag($TEAH_3$)$_2$] (Fig. S7, ESI†) resulting in the formation of a chain structure. Fig. S8 (ESI†) shows a top view of the polymer chain of complex [Ag($TEAH_3$)$_2$] (PIC), extended along the crystallographic '*c*' axis.

3 NMR spectral discussion

NMR spectroscopy can be useful for studying the coordination of various ligating sites in solution phase. However in the present complexes, the ligands THEEN, THPEN and $TEAH_3$ do not seem to be very strong complexing agents in solution form and might get dissociated, as is evident from the appearance of multiplet signals corresponding to methyl and methylene protons in their ^{1}H NMR spectra. The signal corresponding to picrate is more apparent and appears at 8.60 ppm in complexes (**1**) and (**3**) while at 8.61 ppm in complex (**2**) (Fig. S9–S11, ESI†).

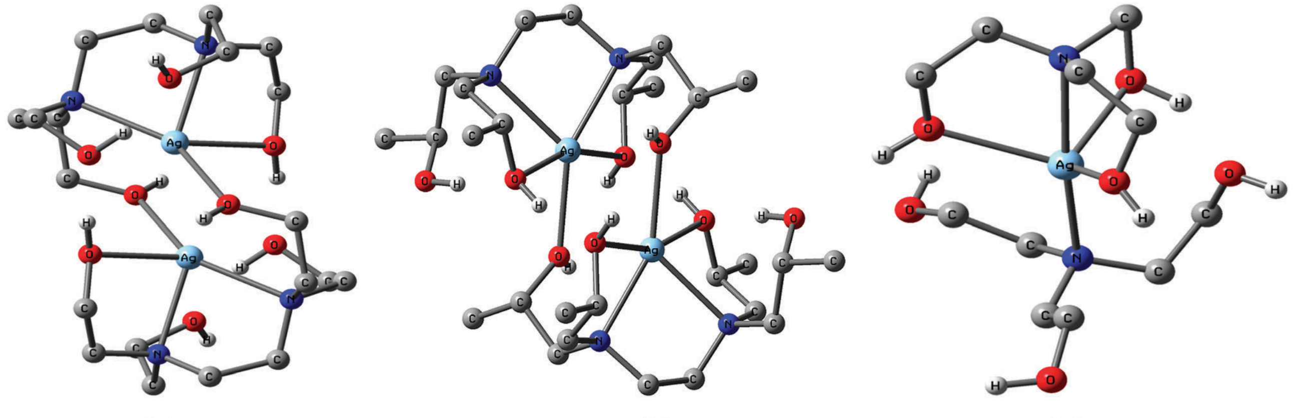
4 Computational discussion

It is appropriate here to correlate the structural parameters obtained from the crystal structure studies with computational data. The structural parameters have been calculated, and the



(a) (b)

Fig. 3 (a) ORTEP diagram of the complex (**3**) with an atom labelling scheme. Picrate anion and the hydrogen attached to the carbon atoms have been omitted for clarity. (b) Distorted trigonal-bipyramidal view of the complex.



(a) (b) (c)

Fig. 4 Optimized geometries: (a) $[Ag(THEEN)]_2(PIC)_2$ (**1**), (b) $[Ag(THPEN)]_2(PIC)_2$ (**2**) (c) $[Ag(TEAH_3)_2](PIC)$ (**3**).

HOMO–LUMO energy gaps have been evaluated by the DFT method. Fig. 4 shows the optimized molecular structures for complexes (**1**), (**2**) and (**3**). Only the primary coordination sphere of the metal ions are optimized. Comparison of the selected bond lengths and bond angles are given in the supplementary information (Table S1, ESI†) as space restrictions do not allow the complete listing of calculated bond lengths, bond angles for the new silver(I) complexes. It is important to mention here that all of the geometric structures were identified and after optimization, tend to reorganise close to the experimental structures.

The optimized geometry analysis reveals that the observed and calculated positions of the metal, ligand, the coordination number and the molecular geometry are in agreement. The energy minimized structures reproduced the observed X-ray structures and a maximum coherence in bond lengths is observed in complex (**2**) (Fig. S13, ESI†). Deviation in the experimental and theoretical bond lengths is less than 0.20 Å for complexes (**1**) and (**2**) of the coordinating atoms, whereas it is slightly higher for complex (**3**) (0.22 Å). The deviation in experimental and theoretical bond distances between two Ag$\cdots$Ag in complex (**1**) is 0.36 Å, whereas in complex (**2**) deviation is very small (0.03 Å). The maximum deviation in the L–Ag–L bond angles is 13.5° for complex (**1**), whereas for complexes (**2**) and (**3**) it is relatively less (6.7° and 4.3°) (Table S1, Fig. S12–S14, ESI†). The small discrepancies in bond lengths and bond angles are attributable to H-bonding and packing interactions within the lattice, which are not modelled during computational studies.

4.1 HOMO–LUMO analyses

The frontier orbitals, HOMO and LUMO take part in chemical reactions. Fig. 5 shows the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) for silver complexes (**1**), (**2**) and (**3**). It has been found that the highest occupied molecular orbital (HOMO) is largely distributed over the amine nitrogens, hydroxyl oxygen atoms and also on the silver(I) ions in complexes (**1**) and (**2**), whereas the (LUMO) is completely delocalized on both the silver(I) ions, amine nitrogens and hydroxyl oxygens for complexes (**1**) and (**2**). The HOMO in complex (**3**) is concentrated on the metal ion as well as on the coordinated hydroxyl oxygen atoms, whereas the LUMO is completely delocalized on the whole complex. The energy gap between the highest occupied and the lowest unoccupied molecular orbitals is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The energy gaps observed for dinuclear complexes (**1**) and (**2**) are 2.530, 2.640 eV respectively and is 1.061 eV for mononuclear complex (**3**) (Table 4). It is pertinent to mention here that these gaps are smaller than the previously reported analogous copper complexes[60] and $[Ag(sac)(Ph_2SNH)]$[61] (Table 4). In general, molecules with smaller energy gaps have unusual optoelectronic properties and electron–transfer phenomena.[62] The title complexes can be made a desirable target for physical studies and electronics applications.

5 Antimicrobial activities

All of the synthesized silver(I) complexes and ligands have been screened on different pathogenic gram −ve (*S. marcescens*, *S. japonicum*, *S. maltophilia*) and gram +ve (*S. aureus*) bacterial strains using the microbroth dilution method and exhibited effective activity against selected bacterial strains with MIC values ranging from 0.7 to 50 μg ml^{-1}, as shown in Table 5. A comparative study of the ligands, metal salt and its complexes indicates that the latter exhibit more antimicrobial activity than the metal salt and ligands against all of the aforementioned bacterial strains, except complex (**3**) against *S. aureus*. It has been found that the ligand $TEAH_3$ and the complex $[Ag(TEAH_3)_2]$ (PIC) (**3**) have equal MIC values against *S. aureus*. Complexes (**1**) and (**2**) have been proven to be more effective and even better antimicrobial agents against *S. aureus*, *S. marcescens* and *S. japonicum* than free picric acid, ligands: THEEN, THPEN, $TEAH_3$ and silver picrate. This proves the fact that the chelation of ligands with metal ions increases the biological activity as reported earlier.[63] Complex (**2**) has been proven to be more

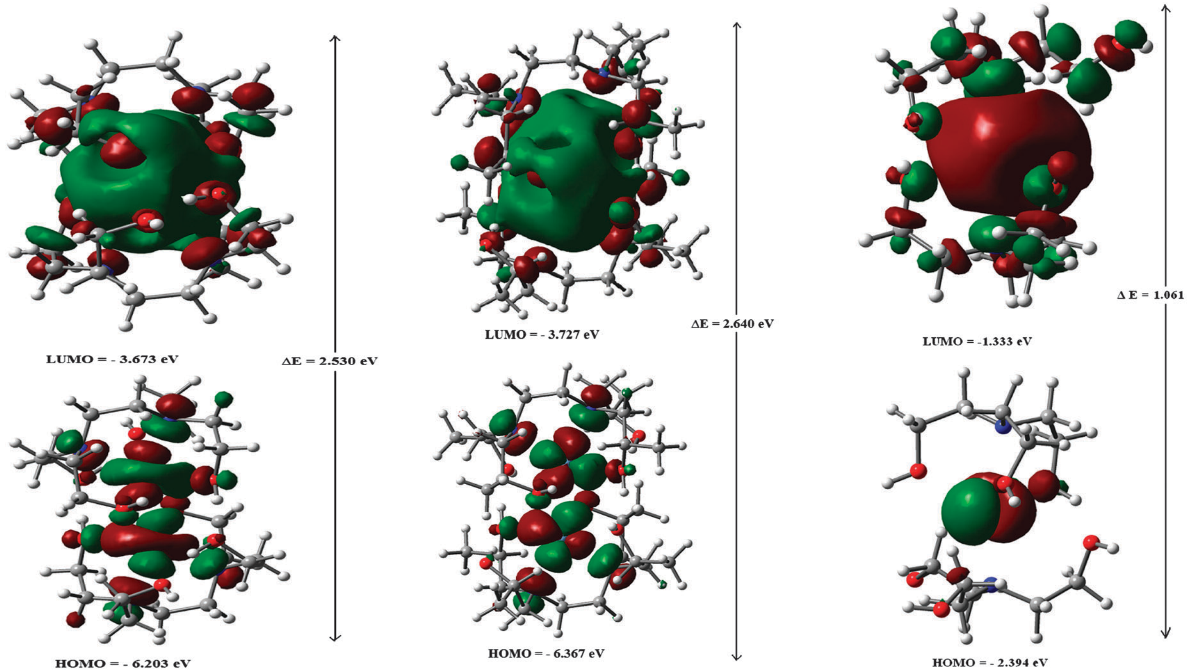


Fig. 5 Frontier molecular orbital surfaces and energy gaps for complexes (**1**), (**2**) and (**3**).

Table 4 HOMO–LUMO energy gaps for the title and previously reported complexes

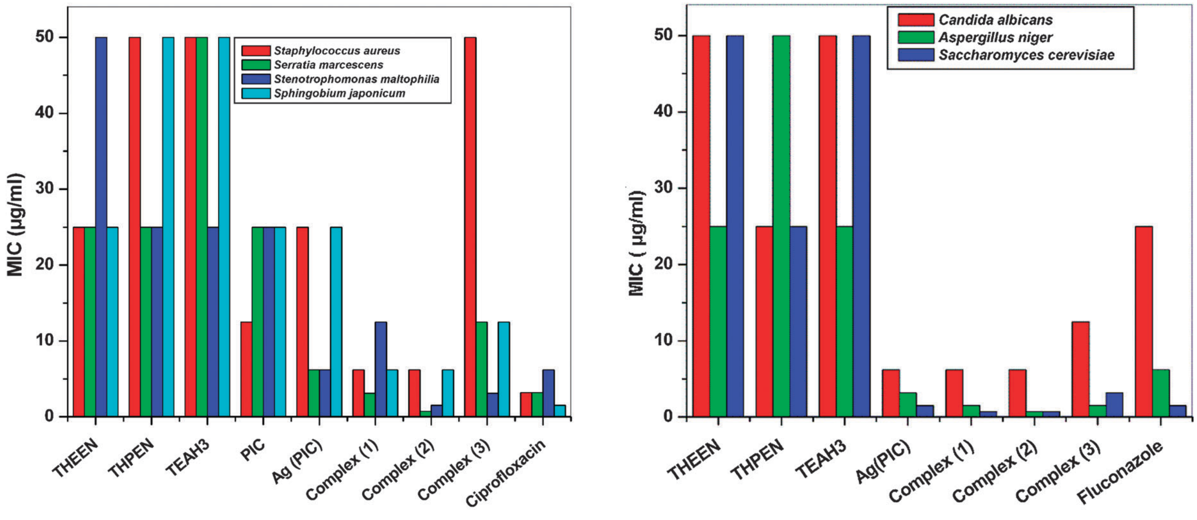
Complexes	HOMO–LUMO energy gap (eV)	Complexes	HOMO–LUMO energy gap (eV)
[Cu(THEEN)(H_2O)]$(PIC)_2$ (**1**)	3.537	[$Ag_2$$(THEEN)_2$] $(PIC)_2$ (**1**)	2.530
[Cu(THPEN)]$(PIC)_2$$C_3H_8O$ (**2**)	3.467	[$Ag_2$$(THPEN)_2$] $(PIC)_2$ (**2**)	2.640
[Cu($TEAH_3$)(PIC)](PIC)·H_2O (**3**)	3.619	[$Ag(TEA)_2$] (PIC) (**3**)	1.061
[Ag(sac)(Ph_2SNH)][61]	4.470		

Table 5 Minimum inhibitory concentrations for the ligands, metal salt and the complexes (μg ml^{-1})

Complexes	*S. aureus*	*S. marcescens*	*S. maltophilia*	*S. japonicum*
THEEN	25	25	50	25
THPEN	50	25	25	50
$TEAH_3$	50	50	25	50
PIC	12.5	25	25	25
Ag(PIC)	25	6.2	6.2	25
Complex (**1**)	6.2	3.1	12.5	6.2
Complex (**2**)	6.2	0.7	1.5	6.2
Complex (**3**)	50	12.5	3.1	12.5
Ciprofloxacin	3.2	3.2	6.2	1.5

effective and even better antimicrobial agents against *S. marcescens* and *S. maltophilia* than standard ciprofloxacin, whereas complex (**1**) is an equally good antimicrobial agent against *S. marcescens* as standard ciprofloxacin (Fig. 6). This may be due to the increased lipophilicity which enhances the penetration of complexes into the lipid membranes and blocks the metal binding sites in the enzymes of microorganisms and they also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts the further growth of organisms.[64,65] Complex (**3**) has a lesser antimicrobial activity against *S. aureus* which might be due to two reasons: (i) *S. aureus* is a gram +ve bacteria which is less susceptible to silver ions than gram −ve bacteria[66] because the former has more peptidoglycan due to its thicker cell wall than the latter. (ii) Complex (**3**) has a mononuclear metal centre, the dinuclear centres are more active than mononuclear centres. As antimicrobial agents the silver(I) picrate complexes follow the order: (**2**) > (**1**) > (**3**). They have exhibited better antimicrobial activity than the previously reported analogues copper picrate complexes *viz.*, [Cu(THEEN)(H_2O)]$(PIC)_2$, [Cu(THPEN)]$(PIC)_2$ C_3H_8O against the aforementioned bacterial strains.[60] [$Ag(TEAH_3)_2$] (PIC) (**3**) is relatively less effective than the corresponding complex of copper *i.e.*, [Cu($TEAH_3$)(PIC)]-(PIC)·H_2O towards gram +ve (*S. aureus)*, gram −ve (*S. marcescens*, *S. japonicum*) and is equally effective towards gram −ve (*S. maltophilia*) bacterial strains.

The ligands, silver picrate and novel complexes of silver(I), have been found to be effective antifungal agents when tested on fungi against *C. albicans*, *A. niger* and *S. cerevisiae* (Table 6, Fig. 6b). Silver picrate and its complexes have been proven to be better antifungal agents than the ligands. The former have relatively lower MIC values than the standard drug (fluconazole) against the aforementioned fungal strains except complex (**3**) against *S. cerevisiae*.



(a) (b)

Fig. 6 (a) Antimicrobial and (b) antifungal activities of the ligands, metal salt and complexes with the minimum inhibitory concentrations (MIC) in (µg ml^{-1}).

Table 6 Minimum inhibitory concentrations for the complexes and the metal salt (µg ml^{-1})

Complexes	*Candida albicans*	*Aspergillus niger*	*Saccharomyces cerevisiae*
THEEN	50	25	50
THPEN	25	50	25
TEAH$_3$	50	25	50
Ag(PIC)	6.2	3.2	1.5
Complex (**1**)	6.2	1.5	0.7
Complex (**2**)	6.2	0.7	0.7
Complex (**3**)	12.5	1.5	3.2
Fluconazole	25	6.2	1.5

Silver picrate salt has been proven to be better or an equally effective antimicrobial agent as a standard drug against the selected fungal species. Silver carbene and water–soluble silver complexes {[Ag(Hhis)]0.2Et(OH)}$_2$, [Ag(Hpyrrld)]$_2$ have been tested earlier on the same fungal species.[27,28] Silver(I) complexes have been found to be very effective antifungal (Table 6, Fig. 6b) and antibacterial agents, but are better antifungal than antibacterial agents.

6 Conclusions

The synthesis, crystal structures, DFT, and antimicrobial studies of complexes [Ag$_2$(THEEN)$_2$](PIC)$_2$ (**1**), [Ag$_2$(THPEN)$_2$](PIC)$_2$ (**2**) and [Ag(TEAH$_3$)$_2$](PIC) (**3**) have been reported. Complexes (**1**) and (**2**) are dinuclear, whereas complex (**3**) is mononuclear. Complex (**1**) has adopted a see-saw geometry with coordination number four, whereas complexes (**2**) and (**3**) have adopted distorted square-pyramidal and trigonal-bipyramidal geometry with coordination number 5. The three novel complexes of silver(I) have been found to be charge-separated in nature. The longer distances between the two Ag···Ag in the dinuclear complexes (**1**) and (**2**) indicates the existence of van der Waals contact between the two silver(I) ions. Extensive hydrogen bonding interactions have been found in all three complexes. Structural parameters from crystallographic and DFT studies have been put together and found to be coherent with each other. The accuracy of the results predicts that the DFT studies performed at the B3LYP/LANL2DZ level is the appropriate quantum chemical method for reproducing the experimental results for the title complexes. The small discrepancies in geometric parameters are attributable to H-bonding and packing interactions within the lattice which are not modeled during computational study. The calculated HOMO–LUMO energy gaps (HLG) suggest the charge transfer transitions are taking place within the complexes. The HLG are smaller for the mononuclear complex (**3**) relative to the dinuclear complexes (**1**) and (**2**).

All three synthesized silver(I) complexes can be used as antimicrobial agents and potential drugs. In the present work, the chelation of ligands with metal ions has not only increased the biological activity of the title complexes but made them better and more effective antimicrobial agents than standard drugs against some of the selected bacterial strains and fungal species. Dinuclear complexes (**1**) and (**2**) exhibited better antimicrobial activity than the mononuclear complexes. Complexes (**1**) and (**2**) are effective antimicrobial agents even against gram +ve bacteria (*S. Aureus*). All of the three reported silver(I) complexes have the potential to be used as precursors to produce nanomaterials for materials science, biomaterials for therapeutic actions and can be made desirable targets for physical studies and electronics applications in future.

7 Experimental section

7.1 General

7.1.1 Equipment and materials. All of the reagents and chemicals were purchased from commercial sources and used as received without further purification. The ligands THEEN, THPEN and $TEAH_3$ were supplied by Sigma Aldrich and Loba Chemie. Picric acid was used after recrystallization. The IR absorption spectra were recorded in the range of 450–4000 cm^{-1} by means of a Perkin Elemer FT-IR RX I spectrometer with KBr pellets (Sigma Aldrich). C H N elemental analyses were performed using Flash 2000 Organic Elemental Analyzer. ^1H NMR were recorded in DMSO–$CDCl_3$ on the FT NMR Spectrometer model Avance-II 400 (Bruker UK Limited, Banner Lane, Coventry, CV4 9GH) using tetramethylsilane as an internal standard. Antimicrobial studies of the complexes were carried out on pathogenic bacterial strains *Serratia marcescens* (MTCC-97), *Sphingobium japonicum* (MTCC-6362), *Stenotrophomonas maltophilia* (MTCC-2446) and *Staphylococcus aureus* (MTCC-3160), whereas antifungal studies were carried out on *Candida albicans* (183), *Aspergillus niger* (872) and *Saccharomyces cerevisiae* (3090) procured from the Microbial Type Culture Collection (MTCC), Institute of Microbial Technology, Chandigarh.

7.1.2 X-ray crystallography. X-ray crystallographic data was collected on a "Bruker APEX-II CCD" area detector diffractometer using a graphite-monochromatized MoKα (λ = 0.71073 Å) radiation source. All of the crystal structures were solved by direct methods[67] using the program 'SIR-92' and refined by full-matrix least-squares refinement methods based on F^2 using the SHELXL-97 programme.[68] Absorption corrections were applied using multi–scan.[69] All non hydrogen atoms were refined anisotropically. The hydrogen atoms of the hydroxyl groups were located from the difference Fourier synthesis and were refined isotropically with U_{iso} values 1.2 times that of their carrier oxygen atoms, with their distances fixed as 0.84(2) Å. In complex 2, one of the hydroxyl groups (O2) was disordered. The disorder could be resolved by splitting the oxygen atom over two atomic positions with their site occupancies and thermal parameters refined as free variables, with a fixed C–O distance of 1.46(2) Å. All of the other hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times that of the carrier atoms for methylene and phenylene carbons and 1.5 times for the methyl group. The geometry of the complexes and hydrogen bonding were calculated using the PARST[70] programme. All of the drawings of the complexes were made using the ORTEP[71] and MERCURY programs.[72]

7.1.3 Computational details. The quantum chemical calculations (DFT calculations) giving the molecular geometries of the minimum energies and molecular orbitals (HOMO–LUMO) were performed using the Gaussian 03 package.[73] The molecular orbitals were visualized using "Gauss view". The method used was Becke's three-parameter hybrid-exchange functional, the nonlocal correlation was provided by the Lee, Yang and Parr expression, and the Vosko, Wilk, and Nuair 1980 local correlation functional (III) (B3LYP)[74] in gaseous phase. The 6-31G basis set was used for C, N and O. The LANL2DZ basis set[75] and pseudopotentials of Hay and Wadt were used for the Ag atom.[76] The input coordinates were obtained from the crystal structure data. Only the primary coordination sphere of the metal ion in complexes (**1**), (**2**) and (**3**) has been optimized. The structural parameters were adjusted until an optimal agreement between the calculated and experimental structure was obtained throughout the entire range of available structures. The geometries of the complexes are also described by quantum chemical approach using the input coordinate from the crystal structure. The primary coordination sphere of all of the silver(I) complexes has been optimized, structural parameters have been calculated, and energy gaps of the frontier orbitals (HOMO–LUMO) have been determined with the B3LYP/6-31G/LANL2DZ level of theory. The theoretical and crystallographic analyses are put together and found to be in good consistency with each other. The previously reported examples of some silver(I) complexes have used DFT/B3LYP/6-31G/LANL2DZ (Gaussian software) to optimize the molecular geometries of complexes of silver with tryptophan,[43a] *n*-acetyl-l-cysteine,[43b] *S*-*S*-diphenylsulfimide,[61] chloroquine.[77] The same basis set has been used to elucidate the structure of the silver(I) complex with L-buthionine sulfoximine[78] using GAMESS software.

7.1.4 Antimicrobial and antifungal studies. The antimicrobial activity of all of the synthesized silver(I) complexes were investigated against bacterial strains gram −ve (*S. marcescens*, *S. japonicum*, *S. maltophilia*) and gram +ve bacteria (*S. aureus*) using the microbroth dilution[79] method. A broth microdilution susceptibility test was carried out in a 96 well microtitre plate by distributing 240 μl of sterile media and 30 μl of metal complexes solutions ranging from (0.197 μg ml^{-1} to 500 μg ml^{-1}) taking appropriate blanks and controls. Then 30 μl bacterial inocula (organism 10^7 cells per ml) was poured to each well and incubated at 30 °C for 48 hours at 150 rpm in an incubator shaker. The growth was observed in the form of turbidity with naked eyes under light background by comparing the clarity of blank media and the turbidity of the controls. The MICs of the metal complexes were recorded as the lowest concentration where no viability of bacteria was observed in the wells of 96-microwell plates after incubation of 48 h. The growth of the bacteria was measured by observing the minimum inhibitory concentration. DMSO was used as a control, ciprofloxacin and fluconazole as standard drugs for the antimicrobial and antifungal studies.

7.1.5 General methods of synthesis

General Synthesis. Silver(I) picrate was synthesised by making a solution of silver nitrate and picric acid separately in ethanol solution. These solutions were then mixed slowly and warmed. The ratio of silver nitrate and picric acid was kept at 1 : 1. The solution was stirred for 30 minutes and bright yellow coloured crystals of silver(I) picrate were obtained. The melting point of silver(I) picrate was found to be 155 °C. All three silver(I) complexes were prepared by the reaction between silver(I) picrate and the corresponding ligands (THEEN, THPEN and $TEAH_3$) in equimolar quantities (1 : 1) using ethanol as the solvent with stirring for 50 minutes. Then the solution was allowed to evaporate slowly at room temperature. Suitable light yellow colour crystals were obtained after one week for X-ray crystal analysis.

*$[Ag(THEEN)]_2(PIC)_2$ (**1**).* Melting point: 110 °C with grey metallic silver. Yield: 85%. Elemental analysis: anal. calc.

(found) for $C_{32}H_{52}Ag_2N_{10}O_{22}$: C, 33.58 (33.49); H, 4.58 (4.50); N, 12.24 (12.15)%. IR (KBr) cm^{-1}: 3368br (OH), 2951br (C–H), 1631s (C=C), 1561s (NO_2), 1336s (NO_2), 1437br (=CH), 1277s (C–O), 1161s (–OH), 1079 (C–O). ^1H NMR (DMSO-d_6–$CDCl_3$ (1 : 1)): 2.64–2.67 (m, 12H, $6CH_2$), 3.48–3.54 (m, 8H, $4CH_2$), 8.60 (s, 2H, ArCH).

[Ag(THPEN)]$_2$(PIC)$_2$ **(2)**. Melting point: 140 °C. Yield: 65%. Elemental analysis: anal. calc. (found) for $C_{40}H_{68}Ag_2N_{10}O_{22}$: C, 38.23 (38.15); H, 5.45 (5.37); N, 11.15 (11.06)%. IR (KBr) cm^{-1}: 3319br (OH), 2973w (C–H) br), 1610s (C=C), 1567s (NO_2), 1343 *vs.* (NO_2), 1430w (=CH), 1275s (C–O), 1163s (–OH), 1084s (C–O). ^1H NMR (DMSO-d_6–$CDCl_3$ (1 : 1)): 1.10–1.19 (m, 12H, $4CH_3$), 3.84–3.86 (m, 4CH), 2.00–2.98 (m, 12H, $6CH_2$), 8.61 (s, 2H, ArCH).

[Ag(TEAH$_3$)$_2$](PIC) **(3)**. Melting point: 105 °C. Yield: 70%. Elemental analysis: anal. calc. (found) for $C_{18}H_{32}AgN_5O_{13}$: C, 34.08 (34.01); H, 5.08 (5.03); N, 11.04 (10.94)%. IR (KBr) cm^{-1}: 3380br (OH), 2953br (CH), 1631s (C=C), 1561s (NO_2), 1337s (NO_2), 1438br (CH), 1277s (C–O), 1161s (OH), 1075s (CO). ^1H NMR (DMSO-d_6-$CDCl_3$ (1 : 1)): 2.52–2.54 (m, $6CH_2$), 8.60 (s, 2H, ArCH).

Acknowledgements

The authors are highly thankful to the Ministry of Human Resource and Development (MHRD), New Delhi for providing research assistantship to Mr Rakesh Kumar, one of the authors and Dr B R Ambedkar National Institute of Technology, Jalandhar for providing research infrastructure. Rakesh Kumar is also thankful to Joyee Mitra for their kind help during the course of this present work.

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