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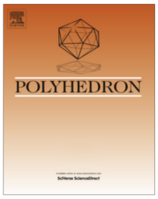

Synthesis, crystal structure determination and antimicrobial studies of copper(II) picrate complexes with N,N,N′,N″-tetrakis(2-hydroxyethyl/propyl) ethylenediamine and tris(2-hydroxyethyl)amine

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ABSTRACT

The present work consist of synthesis, spectroscopic and crystal structure investigations of complexes [Cu(THEEN) (H_2O)] $(PIC)_2$ (**1**), [Cu(THPEN)] $(PIC)_2 \cdot C_3H_8O$ (**2**) and [Cu($TEAH_3$)(PIC)] (PIC)·(H_2O) (**3**) and their application in antimicrobial activities. In these complexes, THEEN is N,N,N′,N″-tetrakis(2-hydroxyethyl) ethylenediamine and THPEN is N,N,N′,N″-tetrakis(2-hydroxypropyl) ethylenediamine, are tetrapodal ligands and $TEAH_3$ is tris(2-hydroxyethyl)amine, a tripodal ligand. Crystal structure investigations have revealed that the coordination number of Cu(II) is five with square pyramidal geometry in complex (**1**) and THEEN is interacting with metal ion through both of its amine nitrogens and two of the four hydroxyl oxygens in a tetradentate manner. The metal ion in complex (**2**) is having a distorted octahedral geometry with coordination number six and THPEN is interacting with it through all ligating sites in a hexadentate way. The picrate anions are present outside the coordination sphere in both of these complexes and are involved in hydrogen bonding interactions resulting in the formation of charge-separated complexes (**1**) and (**2**). The coordination number of Cu(II) is five with square pyramidal geometry in complex (**3**) where the ligand tris(2-hydroxyethyl)amine ($TEAH_3$) is interacting through all of its donor atoms in a tetradentate way. One of the two picrate anions is in coordination with metal ion whereas other is present outside the coordination sphere and is involved in hydrogen bonding interactions resulting in formation of partially charge-separated complex.

1. Introduction

Podands are the acyclic ligands containing potential donor atoms such as oxygen and nitrogen and may be broadly classified as dipodal, tripodal and polypodal ligands [1–4]. They have a tendency to form host- guest complexes with conformational changes due to high degree of flexibility and exhibit rapid complexation and decomplexation kinetics. Hence they rapidly response in sensing applications but possess lower binding constants than their cyclic analogs [5]. These compounds may bind metal ions and other species, catalyze reactions, form novel complex structures of biological relevance and have importance in material science. Vögtle and Weber have examined structural variations and reported a variety of podands with quinoline end groups [6]. An enormous number of podands having a variety of end groups and their complexes with metal ions have been reported in literature.

Here we will specify our discussion to the tripodal ($TEAH_3$) and tetrapodal (THEEN/THPEN) ligands having hydroxyls groups as polar end groups. Here $TEAH_3$ = triethanolamine, H_3 indicates the number of alcohol protons present. Recently Gulcemal and coworkers has reported the structural characterization of complex of Pd(II) with a tetrapodal ligand having hydroxyls as end groups that has proved to be a good catalyst for Suzuki/Miyaura reaction in water [7]. Cu(II) complex of tripodal ligand having hydroxyls as end groups $[O \subset Cu_4(tea)_4(BOH)_4][BF_4]_2$ [8], is also an efficient catalyst for selective oxidation of alkylarenes to phenyl ketones by tert-butylhydroperoxide. Like copper other transition metal ions Mn(II), Co(II), Ni(II), Zn(II), Y(III), Cd(II), Pd(II), Hg(II) [9,10] have also been found to get encapsulated by the pseudocyclic cavity of triethanolamines. Not only transition metal ions but also inner-transition metal ions La(III), Yb(III), Eu(II), Pr(III) [11] and s-block metal ions Li(I), Na(I), Ca(II), Sr(II), Ba(II) [12–14] have been reported to be complexed with triethanolamines under the influence of a variety of anions.

The complexes of some of s-block metal ions Na(I), Ca(II), Sr(II), Ba(II) [15] and a few transition metal ions Cu(II), Ag(I), Ti(IV), Pd(II)

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[16,7] with tetrapodal ligands (THEEN, THPEN) have already been reported in literature. Nature of s-block metal ion complexes was investigated under the influence of picrate, 3,5-dinitrobenzoate, 2,4-dinitrophenolate and o-nitrobenzoate and found to be forming charge-separated complexes with the exception of Ba(THPEN)(PIC)$_2$ and Ca(THEEN)(H$_2$O)$_2$ (DNP)$_2$·H$_2$O forming ion-paired complexes whereas [Ca(THEEN)(PIC)](PIC) formed partially charge-separated complexes [15]. Earlier crystal structure of copper with THPEN and THEEN ligands has been investigated under the influence of perchlorate anions [16a,b]. The present work consists of the synthesis of copper complexes (**1**–**3**) with both tetrapodal ligands (THEEN and THPEN) and a tripodal ligand (TEAH$_3$) under the influence of picrate as counter anions. The structural characterizations are carried out by using X-ray crystallography as a tool and the antimicrobial studies have been investigated using microbroth dilution method.

2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents used in this study were of high purity. The ligands THEEN, THPEN and TEA were supplied by Sigma Aldrich and used without purification. Picric acid was used after purification. The IR absorption spectra were recorded in the range of 450–4000 cm^{-1} by using Perkin Elemer FT-IR RX I spectrometer with KBr pellets (Sigma Aldrich). The elemental analyses were performed on Flash 2000 Organic Elemental Analyzer. For antimicrobial activity, pathogenic bacteria *Serratia marcescens* (MTCC-97), *Sphingobium japonicum* (MTCC-6362), *Stenotrophomonas maltophilia* (MTCC-2446) and *Staphylococcus aureus* (MTCC-3160) were procured from Microbial Type Culture Collection (MTCC), Institute of Microbial Technology, Chandigarh. All the glass wares and materials to be used for antimicrobial activity were sterilized in an autoclave.

2.2. X-ray crystallographic study

X-ray crystallographic data was collected on "Bruker APEX-II CCD" area detector diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) source. The crystal structures were solved by direct method [17] using the program SIR-97 and refined by full-matrix least-squares refinement methods based on F^2, using SHELXL-97 programme [18]. All the CH$_2$ hydrogens were attached geometrically except for those bonded to hydroxyl oxygens and water molecules which were located from difference Fourier maps. None of these hydrogen were refined, were made to ride on their respective atoms. Molecular structures of the complexes were drawn with the help of ORTEP programme [19]. Calculation of hydrogen bonding were performed using PARST [20].

2.3. Synthesis

2.3.1. [Cu(THEEN)(H$_2$O)] (PIC)$_2$ (**1**)

The complex (**1**) was synthesized by dissolving copper (II) picrate (0.521 g, 0.001 mol) and THEEN (0.236 g, 0.001 mol) in an aqueous solution. The mixture was stirred for 1 h at 50 °C and then left to cool down at room temperature. Change in color of the solution indicated that the reaction has occurred. The green crystals were obtained after 48 h at room temperature. Recrystallization was carried out by slow evaporation in a mixture of water and methanol. The decomposition of the product was found to be in the range 170–195 °C. Yield: 80%. IR (KBr) cm^{-1}: 3447 (ν (OH, br)), 2903 (ν (C–H) br), 1632 (ν (=CH) str), 1560 (ν (NO$_2$) as, str), 1335 (ν (NO$_2$) s, str), 1437 (δ (=CH) w, br), 1277 (ν (C–O) str), 1163 (δ (–OH) s), 1078 (ν (C–O) alcohol), 937 (δ (=C–H) bend),

Table 1
Summary of the crystal structure, data collection and structure refinement parameters for complexes (**1**–**3**).

Complexes	**1**	**2**	**3**
Empirical formula	$C_{22}H_{30}CuN_8O_{19}$	$C_{29}H_{44}CuN_8O_{19}$	$C_{18}H_{21}CuN_7O_{18}$
Formula weight	774.09	872.27	686.96
Crystal system	triclinic	triclinic	triclinic
Crystal size	0.19 × 0.09 × 0.07	0.19 × 0.17 × 0.14	0.13 × 0.10 × 0.09
Color	green	green	light green
Shape	needle	rectangular	needle
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.299(5)	12.149(5)	8.070 (5)
b (Å)	14.281(5)	12.363(5)	12.664(5)
c (Å)	15.814(5)	14.667(5)	13.061(5)
α (°)	104.004(5)	99.061(5)	86.605(5)
β (°)	91.535(5)	110.000(5)	89.592(5)
γ (°)	100.283(4)	103.598(5)	72.106(5)
V (Å^3)	1569.5(13)	1942.6(13)	1267.9(11)
Z	2	2	2
$\rho_{calc.}$ (g cm^{-3})	1.638	1.491	1.799
μ (cm^{-1})	0.793	0.650	0.966
$F(000)$	798.0	910.0	702.0
θ Range of data collection	1.33°–24.23°	1.53°–30.32°	1.69°–31.90°
Limiting frequency	$-8 < h < 9$	$-16 \leqslant h \leqslant 17$	$-4 \leqslant h \leqslant 11$,
	$-18 < k < 18$	$-17 \leqslant k \leqslant 17$	$-17 \leqslant k \leqslant 18$
	$-20 < l < 20$	$-20 \leqslant l \leqslant 20$	$-18 \leqslant l \leqslant 19$
Total reflections	32 389	43 035	8412
Independent reflections	7397[$R_{int} = 0.0521$]	11456[$R_{int} = 0.0219$]	6876 [$R_{int} = 0.0154$]
Completeness to theta = 25.00	95.4%	98.1%	78.9%
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 (GOF) on F^2	1.021	1.038	1.040
Final R indices [$I > 2$ (I)]	$R_1 = .0610$ $wR_2 = 0.1725$	$R_1 = 0.0676$, $wR_2 = 0.1920$	$R_1 = 0.0418$, $wR_2 = 0.0956$
R indices (all data)	$R_1 = .1008$ $wR_2 = 0.1983$	$R_1 = 0.0880$, $wR_2 = 0.2128$	$R_1 = 0.0624$, $wR_2 = 0.1065$
Largest diff. peak and hole (e Å^3)	1.042 and −1.060	1.431 and −0.735	0.443 and −0.596

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

Bond distances (Å)		Bond angles (°)	
*Complex (**1**)*			
Cu–N1	1.999 (3)	N1–Cu–N2	88.24 (12)
Cu–N2	2.035 (3)	O1–Cu–N1	83.08 (13)
Cu–O1	1.984 (3)	N1–Cu–O2	79.50 (12)
Cu–O2	2.347 (4)	N2–Cu–O2	96.19 (12)
Cu–O1W	1.942 (3)	O1W–Cu–N2	97.20 (12)
		O1W–Cu–N1	174.52(12)
		O1W–Cu–O1	91.45(13)
		O1W–Cu–O2	100.51(14)
		O1–Cu–N2	166.64 (13)
		O1–Cu–O2	92.21 (14)
*Complex (**2**)*			
Cu–N1	2.019 (2)	N1–Cu–N2	88.82 (10)
Cu–N2	2.013 (2)	N1–Cu–O2	79.26 (10)
Cu–O1	1.994 (2)	N2–Cu–O2	100.87 (11)
Cu–O2	2.324 (3)	O1–Cu–N1	83.08 (11)
Cu–O3	2.413 (3)	O1–Cu–N2	159.76 (11)
Cu–O4	1.960 (2)	O1–Cu–O2	95.81 (10)
*Complex (**3**)*			
Cu–N1	1.990 (18)	N1–Cu–O1	82.14 (7)
Cu–O1	2.030 (2)	N1–Cu–O2	84.04 (7)
Cu–O2	2.031 (2)	N1–Cu–O3	82.55 (7)
Cu–O3	2.158 (2)	N1–Cu–O4	177.24 (7)
Cu–O4	1.899 (17)	O1–Cu–O2	151.29 (8)
		O1–Cu–O3	97.97 (9)
		O1–Cu–O4	100.61 (7)
		O2–Cu–O3	105.04 (9)
		O2–Cu–O4	93.44 (7)
		O3–Cu–O4	97.06 (7)

Table 3
Selected geometric parameters 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···O1W	0.85	2.776	2.811 (4)	83.49
O1–H1···O5A	0.85	1.822	2.614 (4)	152.52
O1–H1···O11A	0.85	2.305	2.897 (6)	126.28
O2–H2···O3C	0.81	1.889	2.928 (4)	160.37
O3–H3···O12B	0.82	1.819	2.630 (5)	169.24
O4–H4···O12C	0.82	1.997	2.722 (5)	147.08
O1W–H1W···O1	0.83	2.701	2.811 (4)	88.88
O1W–H1W···O5A	0.83	1.954	2.725 (5)	153.41
O1W–H1W···O6A	0.83	2.297	2.868 (6)	126.07
O1W–H2W···O4B	0.83	1.889	2.683 (4)	160.37
*Complex (**2**)*				
O1–H1···O12A	0.93	2.249	2.666 (4)	106.44
O2–H15···O19A	0.93	2.347	2.632 (5)	97.29
O3–H8···O13A	0.93	2.355	2.905 (6)	117.56
O4–H22···O5A	0.93	1.700	2.597 (3)'	160.79
O19–H44···O5	0.82	2.297	2.927 (5)	134.08
O19–H44···O11	0.82	2.237	2.984 (1)	151.74
*Complex (**3**)*				
O1–H1···O11	0.93	1.854	2.629 (3)	138.84
O1–H1···O17	0.93	2.274	2.987 (3)	133.03
O2–H2···O11A	0.93	1.970	2.731 (3)	137.83
O3–H3···O1W	0.93	1.890	2.769 (3)	156.63
O1W–H1W···O17	0.72	2.129	2.907 (4)	161.68
O1W–H2W···O15B	0.76	2.099	2.900 (3)	168.22

795 (δ (=CH), s), 709 (δ (C=C)). Elemental Analysis: *Anal.* Calc. for $C_{22}H_{30}CuN_8O_{19}$: C, 34.13; H, 3.90; N, 14.47. Found: C, 34.16; H, 4.03; N, 15.53%.

*2.3.2. [Cu(THPEN)](PIC)$_2$ C$_3$H$_8$O (**2**)*

The synthesis of complex (**2**) was similar to that of (**1**), but with THPEN (0.292 g, 0.001 mol) in place of THEEN. The dark green color crystalline product obtained and was recrystallization by slow evaporation in water–propanol mixture. Dark green color crystals were obtained after few days. The crystals were decomposed in the range of 175–200 °C. Yield: 76%. IR (KBr) cm^{-1}: 3293 (ν (OH, br)), 2929 (ν (C–H) br), 1631 (ν (=CH) str), 1564 (ν (NO_2) as, str), 1335 (ν (NO_2) s, str), 1435 (δ (=CH) w, br), 1268(ν (C–O) str), 1163 (δ (–OH) s), 1076 (ν (C–O) alcohol), 939 (δ (=C–H) bend), 788 (δ (=CH), s), 709 (δ (C=C)). Elemental analysis: *Anal.* Calc. for $C_{29}H_{44}CuN_8O_{19}$: C, 39.93; H, 5.08; N, 12.85. Found: C, 40.12; H, 4.94; N, 12.78%.

*2.3.3. [Cu(TEAH$_3$)(PIC)](PIC) H$_2$O (**3**)*

The synthesis of complex (**3**) was carried out by dissolving Cu(II) picrate (0.521 g, 0.001 mol) and $TEAH_3$ (0.149 g, 0.001 mol) in an aqueous medium. Change in color of the light green solution to dark green indicated the completion of reaction. The green color crystalline solid was separated out. Recrystallization was carried out in a water–methanol mixture by slow evaporation. The decomposition of the crystals was found to be in the range of 190–200 °C. Yield: 84%. IR (KBr) cm^{-1}: 3354 (ν (OH, str)), 2931 (ν (C–H) s), 1633 (ν (=CH) str), 1560 (ν (NO_2) as, str), 1333 (ν (NO_2) s, str), 1437 (δ (=CH) w, br), 1269 (ν (C–O) str), 1162 (δ (–OH) s), 1080 (ν (C–O) alcohol), 937 (δ (=C–H) bend), 795 (δ (=CH), s), 709 (δ (C=C)). Elemental analysis: *Anal.* Calc. for $C_{18}H_{21}CuN_7O_{18}$: C, 31.47; H, 3.08; N, 14.27. Found: C, 31.50; H, 5.03; N, 14.30%.

3. Antimicrobial activity

In the current study, all the synthesized copper complexes were tested against pathogenic Gram –ve bacteria (*S. marcescens*, *S. japonicum*, *S. maltophilia*) and Gram +ve bacteria (*S. aureus*) using the microbroth dilution [21] method. It is well established high throughput screening method for antimicrobial agent used in clinical laboratories. Microbroth dilution susceptibility test was carried out in 96 well microtitre plate by distributing sterile media 240 and 30 μl of metal complexes solutions ranging from (0.197 to 500 μg/ml) taking appropriate blanks and controls. Then 30 μl bacterial inocula (Organism 10^7 cells/ml) was poured to each well and incubated at 30 °C for 48 h at 150 rpm in incubator shaker. The growth was observed in the form of turbidity with naked eyes under light background by comparing clarity of blank media and turbidity of controls. The MICs of 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 and ciprofloxacin as a standard drug.

4. Results and discussion

4.1. Description of crystal structures

The crystal data and refinement details of three complexes are given in Table 1. Selected bond distances, bond angles and hydrogen bonding geometry are listed in Tables 2 and 3 respectively. The X-ray crystal structure analysis reveals that the molecular structure of complex (**1**) consists of one Cu (II) ion, two picrate anions, one water molecule and THEEN ligand. THEEN coordinates to Cu(II) through two hydroxyl oxygens O1 and O2 and both amine nitrogen atoms N1 and N2 thus behaving as a tetradentate ligand towards the metal ion as shown in (Fig. 1a). One of the site around metal ion is also occupied by water molecule O1W giving rise to the

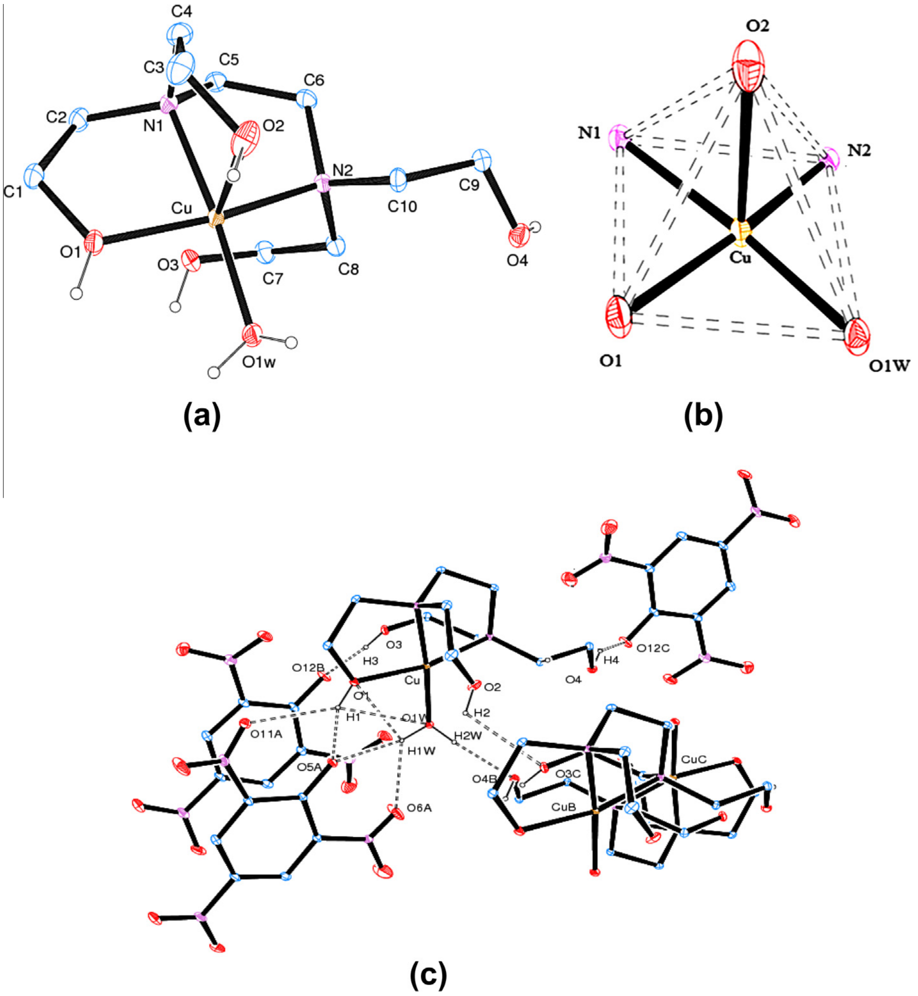

Fig. 1. (a) ORTEP diagram of the complex (**1**), showing the atom labeling scheme. The anions and the hydrogen atoms attached to the carbon atoms have been removed for clarity. (b) Square pyramidal view of the complex. (c) Molecular structure of the complex with hydrogen bonding interactions.

square pyramidal geometry with coordination number five (Fig. 1b). The atoms O1, O1W, N1 and N2 are lying in the equatorial positions forming one plane whereas O2 occurs in axial position above the plane. The two picrate anions do not directly interact with the metal ion but remain outside the coordination sphere.

The complex is thus a charge- separated complex as is in previously reported complexes of calcium picrate [15]. Extensive intermolecular and to a less extent intramolecular hydrogen bonding interactions involving hydroxyl oxygens, water molecule, phenolic oxygen and oxygen of the o-nitro group of picrate anion have been observed in the crystal structure. Solvent water is providing stability to the entire structure by donating and accepting as well as undergoing intermolecular and intramolecular H-bonding interactions (Table 3). It is acting as donor of H-bond towards terminal alcoholic O1 and O4 of the ligand, phenolic O5 and O6 of the nitro group of the picrate ion of the neighboring molecule (Fig. 1c). The terminal alcoholic groups O1, O2 O3 and O4 are donating H- bonds to water molecule (intramolecular), hydroxyl and phenolic oxygens (intermolecular) respectively of the neighboring molecule in the unit cell (Fig. 1c). Besides this, the centre to centre distance between the two phenyl rings is 4.068 Å. This indicates face to face π–π interaction between two phenyl rings.

In complex (**2**), Cu(II) is six coordinated with distorted octahedral geometry. THPEN is interacting with Cu(II) through all the four hydroxyl oxygen and two amine nitrogen atoms of the ligand as shown in (Fig. 2a). Both picrate anions interact indirectly with the metal ion and remain outside the coordination sphere resulting in the formation of a charge-separated complex. Coordinated ligating atoms O2, O3, O4 and N1 of the ligand are present in the equatorial positions and form one plane whereas O1 and N2 lying on the axial positions above and below the plane (Fig. 2b). The lattice solvent molecule propanol is also present outside the coordination sphere in the complex and is involved in intramolecular as well as intermolecular hydrogen bonding interactions (Table 3). The former are displayed when propanol donates its H-bond to phenolic oxygen and one of the oxygen of the nitro group of picrate anion and the latter are observed when it accepts H-bond from terminal alcoholic group O2 of the neighboring unit. All hydroxyl oxygens O1, O2, O3 and O4 of the ligand THPEN are donating H- bonds to phenolic oxygen and one of the oxygen of the nitro group of the neighboring picrate anions making them acceptors of H-bonds in an intermolecular way, thus connecting the neighboring units together and stabilizing the molecular structure (Fig. 2c). In this complex the two phenyl rings have centre to centre distance 3.699 Å and they are also facing each other with π–π interaction.

The final X-ray crystal structure of complex (**3**) is shown in (Fig. 3a) in which all the donor sites of TEAH$_3$ ligand O1, O2, O3, N1 and phenolic oxygen O4 of the picrate anion is in coordination sphere of the Cu(II) ion with square pyramidal geometry (Fig. 3b). The other picrate anion does not directly interact with the metal ion but remains outside the coordination sphere thus resulting in the formation of a partially charge-separated complex. One lattice

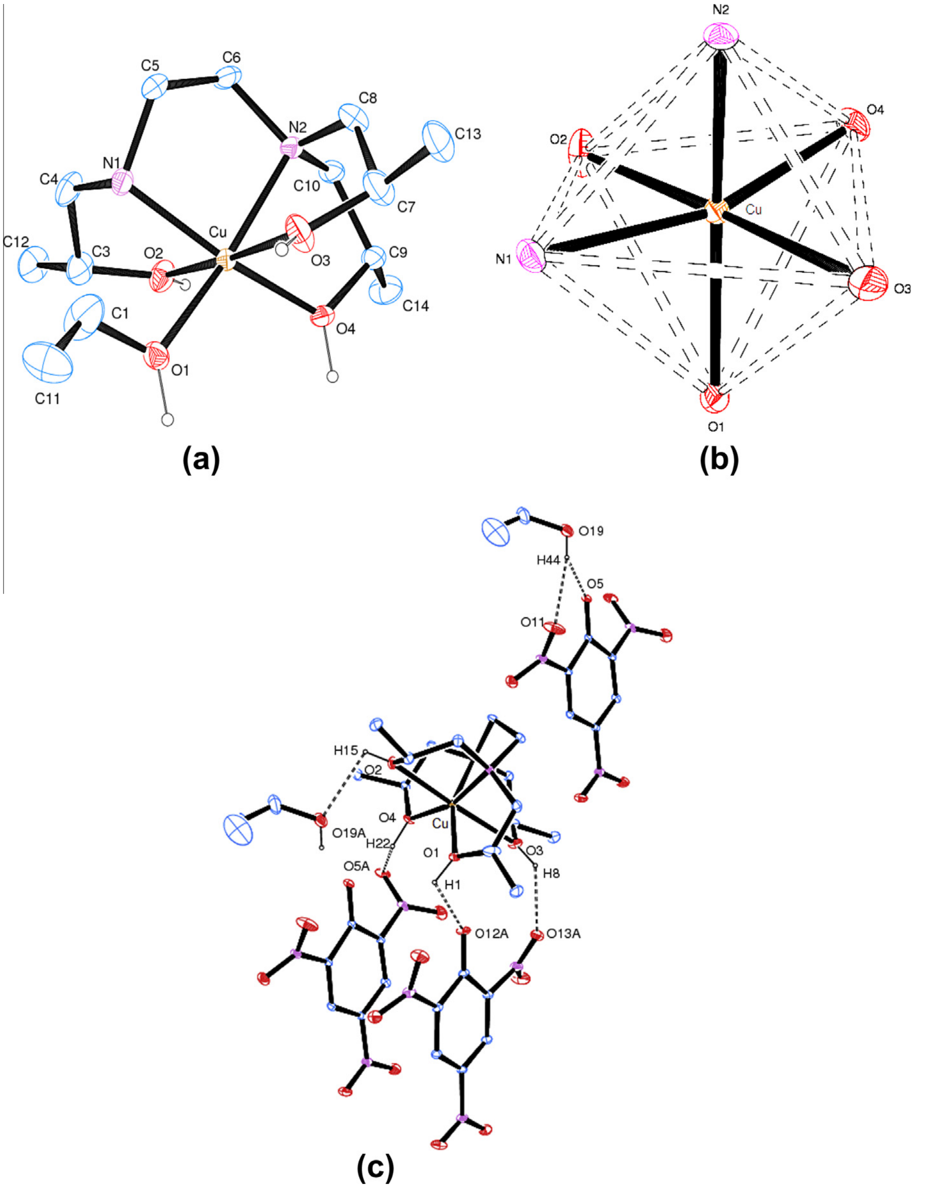

Fig. 2. (a) ORTEP diagram of the complex (**2**), showing the labeling scheme. The anion and the hydrogen atoms attached to the carbon atoms have been removed for clarity. (b) Distorted octahedral view of the complex. (c) Molecular structure of the complex with hydrogen bonding interactions.

water molecule is also present outside the coordination sphere of the metal ion and is involved in extensive intermolecular and intramolecular hydrogen bonding interactions by donating its H-bonds towards O15 and O17 oxygens of the neighboring picrate molecule respectively. It is also accepting H-bond from terminal alcoholic oxygen O3 in an intramolecular way. O1 and O2 of TEAH$_3$ are donating H-bonds to one of the picrate anion in an intermolecular as well as intramolecular way respectively (Fig. 3c). Thus, all the terminal hydroxyl oxygens of the ligand are acting as donors of H-bonds. In this complex, the centre to centre distance between the two phenyl rings is 4.210 Å that indicates face to face π–π interaction between two phenyl rings.

The number of hydrogen bonds formed in the complexes (**1**) and (**3**) are greater in comparison to the complex (**2**) and it may be due to the presence of water molecule either in the inner or outer coordination sphere forming the intermolecular hydrogen bonding.

Both tetrapodands THEEN and THPEN have six potential donor sites whereas tripod TEAH$_3$ has four donor atoms. These ligands adopt different modes of coordination towards the metal ion due to their flexible behavior. Due to more steric crowding, wrapping of tetrapodands [15] around the metal ion does not leave space for larger anions to enter inside the coordination sphere of metal ion resulting in the formation of charge-separated complexes (**1**) and (**2**). Tripodand TEAH$_3$ is having comparatively lesser steric crowding and wraps around the metal ion in such a way that the larger anions can enter the coordination sphere of the metal ion resulting in the formation of partially charge-separated complex (**3**) as is observed in previously reported complexes of barium [12d,13a].

5. Antimicrobial activity

In the current study, all synthesized copper complexes have been tested on different pathogenic bacteria *S. marcescens*, *S. japonicum*, *S. maltophilia* and *S. aureus* using the microbroth dilution method. All complexes showed good activity against bacterial strains with MIC value ranging from 3.2 to 50 μg/ml as shown in

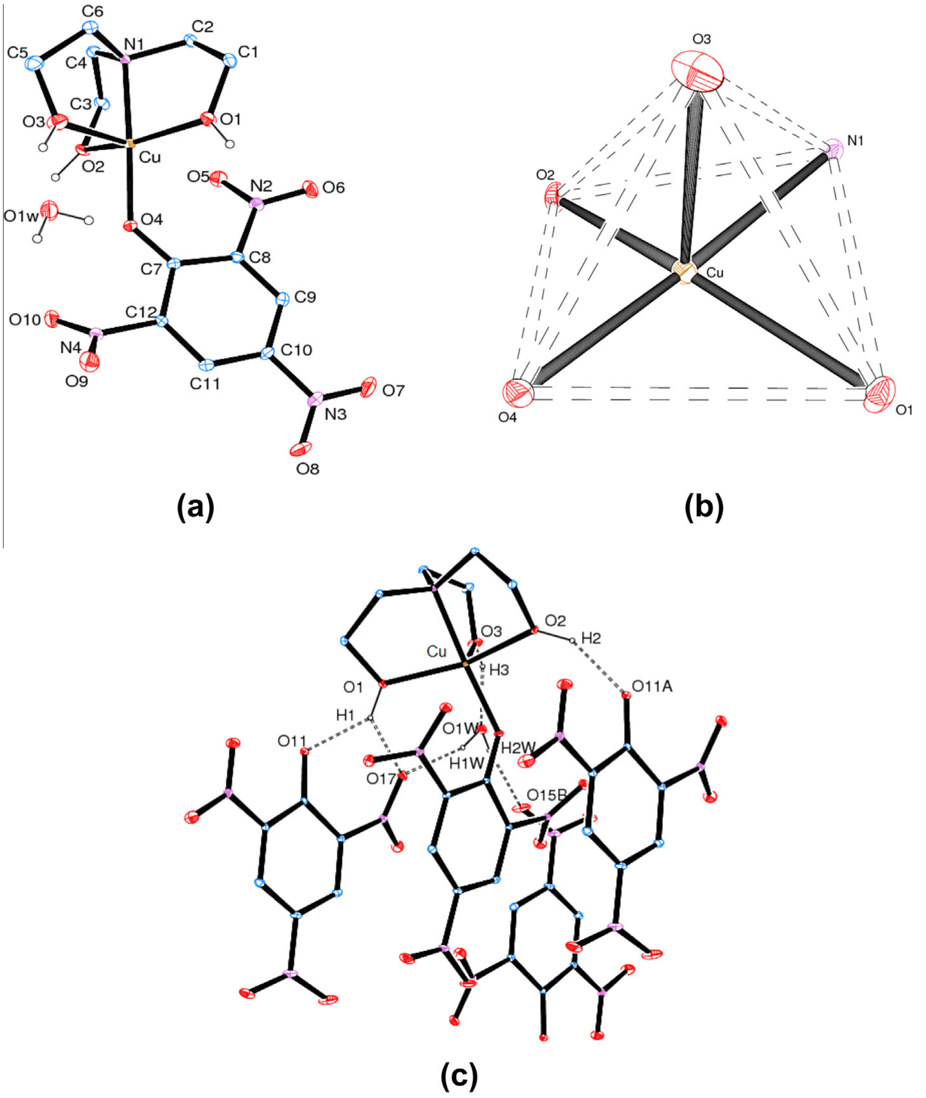

Fig. 3. (a) ORTEP diagram of the complex (**3**), showing the atom labeling scheme. The anion and hydrogen atoms attached to the carbon atoms have been removed for clarity. (b) Square pyramidal view of the complex. (c) Molecular structure of the complex with hydrogen bonding interactions.

Table 4
Minimum inhibitory concentrations for the complexes and the metal salt (μg/ml) on bacterial strains by microbroth dilution method.

Compounds	*Staphylococcus aureus*	*Serratia marcescens*	*Stenotrophomonas maltophilia*	*Sphingobium japonicum*
PIC	12.5	25	25	25
Cu(II)PIC	6.2	12.5	12.5	6.2
Complex (**1**)	50	6.2	6.2	6.2
Complex (**2**)	25	12.5	3.2	6.2
Complex (**3**)	6.2	6.2	3.2	12.5
Ciprofloxacin	3.2	3.2	6.2	1.5

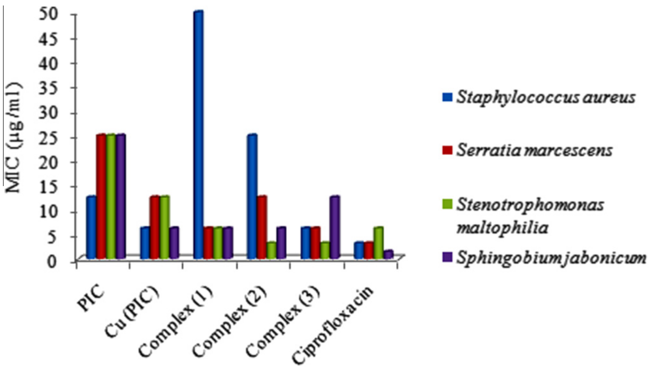

Fig. 4. Antimicrobial activity of complexes with minimum inhibitory concentration (MIC) in (μg/ml).

Table 4. The result revealed that complex (**3**) appeared to have broad spectrum as it exhibits mild to moderate activity towards most of strains and it is comparable to the standard drug ciprofloxacin. This may be due to the enhanced penetration of complexes into the lipid membranes, the hydrocarbon tail function as a lipophillic group to drive the compound through the semipermeable membrane of the cell and blocks the metal binding sites in the enzymes of micro-organism [22]. This study suggests that such type of complexes can further be explored as specific anti bacterial drugs due to their decent activity against studied bacterial strains. The bacterial growth inhibition capacity of the complexes followed the order: (**3**) > (**1**) > (**2**) as shown in Fig. 4.

From the antimicrobial study we have observed that, chelation of the ligands with the metal ions also serve as useful tool for the design of potential antimicrobial agents.

6. Conclusions

Crystal structure determinations reveal that all the three complexes of Cu(II) picrate have been crystallized with $P\bar{1}$ space group. Coordination number of copper is five in complexes (**1**) and (**3**) with square pyramidal geometry and six in complex (**2**) with distorted octahedral geometry. The interaction of tetrapodands with copper picrate results in the formation of charge-separated complexes while interaction of tripodand ($TEAH_3$) results in the formation of partially charge-separated complex. Solvent molecules are present in each of three complexes providing stability to the entire molecules by displaying intermolecular and intramolecular hydrogen bonding interactions and connecting neighboring chains together. Besides this $\pi–\pi$ interaction have also been observed in all the three complexes. These complexes have powerful antimicrobial effect with bacterial growth inhibition capacity followed the order: (**3**) > (**1**) > (**2**). This study suggests that such type of complexes can further be explored as specific anti bacterial drugs due to their decent activity against studied bacterial strains. Future prospective of these complexes is to explore their tendency as efficient and non-hazardous catalyst for catalyzing some chemical reactions.

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Appendix A. Supplementary data

CCDC 881216, 894385 and 880408 contain the supplementary crystallographic data for complexes $[Cu(THEEN)(H_2O)](PIC)_2$ (**1**), $[Cu(THPEN)](PIC)_2\cdot C_3H_8O$ (**2**) and $[Cu(TEAH_3)(PIC)](PIC)(H_2O)$ (**3**) respectively. 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.poly.2013.03.043.

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