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Magnetic, spectroscopic, structural and biological properties of mixed-ligand complexes of copper(II) with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and polypyridine ligands

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Abstract

Two new mixed ligand complexes of copper(II) with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and polypyridine ligands have been prepared and characterized by means of spectroscopic, magnetic and single-crystal X-ray diffraction methods. These two complexes are isomorph and isostructure in which the coordination polyhedron about the copper(II) ion is distorted square pyramidal. $[Cu(PMDT)(bipy)]^{2+}$ and $[Cu(PMDT)(phen)]^{2+}$ show an absorption wavelength maximum at 625 and 678 nm, respectively, assigned to the d–d transition. Antibacterial, antifungal and superoxide dismutase activities of these complexes have also been measured. It was observed that $[Cu(PMDT)(bipy)](ClO_4)_2$ was more effective against *P. Pyocyanea* and *Klebsiella* sp. than *S. aureus.* Similarly, *Fusarium sp.* was highly susceptible against $[Cu(PMDT)(bipy)](ClO_4)_2$ but less susceptible against $[Cu(PMDT)(phen)](ClO_4)_2$.

1. Introduction

Mixed ligand complexes play an important role in biological process as exemplified by many instances in which enzymes are known to be activated by metal ions [1,2]. Copper is an important trace element for plants and animals [3,4] and is involved in mixed ligand complex formation in a number of biological processes [5–7]. Copper(II) complexes have found possible medical uses in the treatment of many diseases including cancer [8,9]. These copper(II) complexes containing polypyridine ligand like 1,10-phenanthroline have shown to be useful photophysical and chemical probes of DNA in view of their relevance to various biochemical and biomedical applications [10–13]. Also the synthesis of such low molecular weight copper(II) complexes mimicking the SOD activity has also been challenging for bioinorganic chemists and for many years efforts have been made to obtain compounds with high catalytic activity [14–38].

N,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDT) is a tridentate nitrogen donor ligand with donor groups suitably placed for forming two 5-membered chelate rings. Such tridentate ligands are known to form binuclear copper(II) complexes which have been a subject of extensive studies, especially with regard to the nature of their spin–spin interaction. 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) chelators also act as potential antitumor agents [39,40]. They can have even better antitumor activity if their hydrophilic groups are masked by copper ions to form water-soluble neutral

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chelates. These neutral chelates are expected to be more permeable through the cell membrane [41,42]. The antitumor activity of these complexes has been suggested to be due to their superoxide scavenging ability [43]. Therefore, we report here the synthesis, magnetic, superoxide, structural and biological properties of mixed ligand complexes of copper(II)- *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine with 2,2′-bipyridine and 1,10-phenanthroline.

2. Experimental

2.1. Materials

Commercial reagents were used as obtained without further purification. Solvents were purified by standard methods before use.

2.2. Magnetic measurements

Magnetic data were collected in room temperatures on a Gouy balance using mercury(II) tetrathiocynatocobaltate(II) ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. unit) as calibrant. The molar susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal constants.

2.3. Spectrometry

EPR spectra were recorded at 77 K on a Varian E-line Century Series EPR spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. Tetracynoethylene was used as field marker ($g = 2.00277$).

The electronic absorption spectra of the complexes were recorded in 100% DMSO solution using Shimadzu UV–Vis 160 Spectrophotometer.

2.4. Bioactivity

Antimicrobial (antibacterial and antifungal) and superoxide dismutase (SOD) activities were evaluated using the following methods.

2.4.1. Antimicrobial activity measurement

The in vitro antimicrobial (antibacterial) activities of these complexes were tested using paper disc diffusion method [44]. The chosen strains were *Pseudomonas pyocyanea*, *Staphylococcus aureus*, *Klebsiella acrogens*, *Rhizopus* sp., *Aspergilles flavus* and *Fusarium* sp. The liquid medium containing the bacterial subcultures was autoclaved for 20 min at 121 °C and at 15 lb pressure before inoculation. The bacteria were then cultured for 24 h at 36 °C in an incubator. Nutrient agar was poured onto a plate and allowed to solidify. The test compounds (DMSO solutions) were added dropwise to a 10 mm diameter filter paper disc placed at the center of each agar plate. The plates were then kept at 5 °C for 1 h, then transferred to an incubator maintained at 36 °C. The width of the growth inhibition zone around the disc was measured after 24 h incubation. Four replicas were made for each treatment. Fungal cultures were isolated from various plant cultures and were maintained on czpeck's agar slants [44,45]. The fungi were isolated on rosebengal medium and stored at room temperature.

2.4.2. SOD activity

In vitro SOD activity was measured using alkaline DMSO as a source of superoxide radical (O_2^-) and nitroblue tetrazolium (NBT) as O_2^- scavenger [37,46]. In general, 400 μl sample to be assayed was added to a solution containing 2.1 ml of 0.2 M potassium phosphate buffer (pH 8.6) and 1 ml of 56 μM NBT. The tubes were kept in ice for 15 min and then 1.5 ml of alkaline DMSO solution was added while stirring. The absorbance was then monitored at 540 nm against a sample prepared under similar condition except that NaOH was absent in DMSO. A unit of superoxide dismutase [SOD] activity is the concentration of complex or enzyme, which causes 50% inhibition of alkaline dimethylsulphoxide (DMSO) mediated reduction of nitroblue tetrazolium chloride (NBT).

2.5. Synthesis

2.5.1. [Cu(PMDT)(bipy)](ClO4)2

In methanol–acetonitrile medium (5:1 v.v.), solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.740 g, 2.0 mmol), PMDT(0.348 g, 2.0 mmol) and 2,2′-bipyridine (0.312 g, 2.0 mmol) were mixed, stirred well and contents were left overnight. The blue crystals of $[Cu(PMDT)(bipy)](ClO_4)_2$ thus formed were obtained and were washed with ethanol and dried in vacuo at room temperature, yield 60%. This gives the satisfactory elemental analysis: Calc. C, 38.52; H, 5.23; N, 11.82; Cu, 10.73. Found: C, 37.92; H, 4.90; N, 11.92; Cu, 11.03%. Ms spectra of this complex show the base peak at *m*/*z* 393.03 (M^+).

2.5.2. [Cu(PMDT)(phen)](ClO4)2

This complex was prepared by similar method, yield 65%. This gives the satisfactory elemental analysis: Calc. C, 40.93; H, 5.03; N, 11.36; Cu, 10.32. Found: C, 40.96; H, 5.24; N, 11.16; Cu, 11.35%. Ms spectra of this complex show the base peak at *m*/*z* 416 (M^+).

2.6. Crystal structure determination

A blue irregular prismatic crystal of $[Cu(PMDT)(bipy)](ClO_4)_2$ and $[Cu(PMDT)(phen)](ClO_4)_2$ was mounted on a glass fiber and used for data collection. Crystal data were collected at 293(2) K, using a Bruker

SMART CCD 1000 diffractometer. Graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used throughout. The data were processed with SAINT [47] and corrected for absorption using SADABS (transmission factors: 1.000–0.117 and 1.000–0.833, respectively) [48]. The structure was solved by direct methods using the program SHELXS-97 [49] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [50]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms. Hydrogen atoms were included in geometrically idealized positions employing appropriate riding models with isotropic displacement parameters constrained to 1.2 U∼(eq) of their carrier atoms. Atomic scattering factors from "International Tables for Crystallography" [51]. Criteria of a satisfactory complete analysis were the ratios of rms shift to standard deviation less than 0.001 and no significant features in final difference maps. The drawing of the molecules was realized with the help of PLATON [52] and SCHAKAL [53].

3. Results and discussion

3.1. Synthesis

These complexes were prepared by reacting equimolar quantities of the copper perchlorate hexahydrate salt, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and 2,2′-bipyridine or 1,10-phenanthroline in methanol-acetonitrile mixed solvent (5:1). These complexes are stable at ambient conditions. Both complexes gave satisfactory elemental analysis.

3.2. Magnetic moment

The magnetic susceptibility measurements in the solid state show that the present complexes are paramagnetic at room temperature. The observed magnetic moments of these complexes are quite close to the values expected for copper(II) complexes without interaction. The magnetic moment values of $[Cu(PMDT)(phen)](ClO_4)_2$ and $[Cu(PMDT)(bipy)](ClO_4)_2$ are 1.83 and 1.85 B.M., respectively. Magnetic moment values ($\mu_{eff.}$) lie within the range normally found for other copper(II) complexes [54,55].

3.3. Spectral studies

X-band EPR spectra of the complexes were recorded in polycrystalline state and also in 100% DMSO. EPR spectra of polycrystalline samples show similar features at room temperature and at liquid nitrogen temperature. The $g = 2$ signal for both the complexes is broad and nearly isotropic. This is suggestive of the presence of spin–spin interaction which may be only intermolecular type arising due to solid effect. Both complexes do not show half field ($\Delta Ms = 2$) signal at RT and LNT. The one electron paramagnetic mononuclear copper(II) complexes display X-band EPR spectra in 100% DMSO at 77 K giving $g_{\|} > g_{\perp} > 2.0023$, indicating a $\{d_x^2–d_y^2\}$ ground state [56] in a square pyramidal geometry. The measured $g_{\|}$ and $g_{\perp}$ values for $[Cu(PMDT)(bipy)](ClO_4)_2$ are 2.254 and 2.063, respectively. Similarly, $g_{\|}$ and $g_{\perp}$ values for $[Cu(PMDT)(phen)](ClO_4)_2$ are 2.251 and 2.065, respectively. The spectra showed well-resolved EPR signals arising out of $M_I = +3/2$ component of copper giving a $A_{\|}$ value of 187 ± 2 G, suggesting a minor distortion in the square pyramidal geometry [57,58]. No nitrogen super hyperfine splitting could be observed. The spectral features are similar to those reported for copper(II)–polyamine complexes [33,59].

Visible spectra of these complexes have been recorded in 100% DMSO solution. $[Cu(PMDT)(bipy)]^{2+}$ and $[Cu(PMDT)(phen)]^{2+}$ complexes show a d–d band in 100% DMSO at 625 nm ($\varepsilon = 258$ dm^3 mol^{-1} cm^{-1}) and 678 nm ($\varepsilon = 277$ dm^3 mol^{-1} cm^{-1}) (Fig. 1), respectively. These absorption maximums are assigned to d–d transition. This difference between two values of λ_{max} may be due to different basicities of ligands, bipy and phen. On the other hand, the bands at ∼260 nm (not shown in Fig. 1) can be assigned to the n–π^*/π–π^* transition of the diethylenetriamine chromophore. The spectra are consistent with square pyramidal geometry.

3.4. Crystal structure

Complexes $[Cu(PMDT)(phen)](ClO_4)_2$ and $[Cu(PMDT)(bipy)](ClO_4)_2$ are characterized by single crystal X-ray diffraction method. The crystal data and structure refinement parameters are given in Table 1 and selected bond angles and bond distances are given in Tables 2 and 3. The structure of the two complexes $[Cu(PMDT)(phen)]^{2+}$ and $[Cu(PMDT)(bipy)]^{2+}$ is quite similar. The coordination geometry in the complexes is distorted square pyramidal. Complex [Cu(PMDT)-

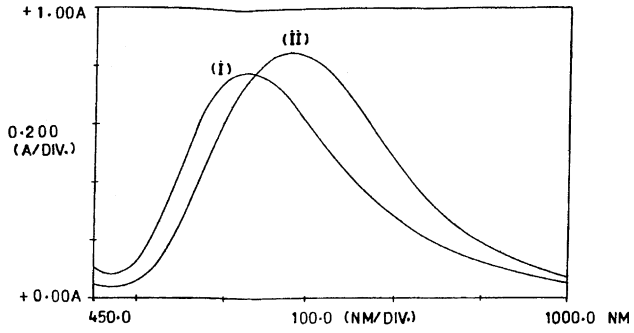

Fig. 1. The electronic spectra (0.003 mol^{-1} dm^{-3}) of (I) $[Cu(dien)(bipy)](ClO_4)_2$ and (II) $[Cu(PMDT)(phen)](ClO_4)_2$ complexes.

Table 1
Crystal data and structure refinement for complexes [Cu(PMDT)(bipy)]$(ClO_4)_2$ and [Cu(PMDT)(phen)]$(ClO_4)_2$

Empirical formula	$C_{19}H_{31}Cl_2CuN_5O_8$	$C_{21}H_{31}Cl_2CuN_5O_8$
Formula weight	591.93	615.95
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group (no. 14)	monoclinic, $P2(1)/c$	monoclinic, $P2(1)/c$
Unit cell dimensions		
a (Å)	11.301(2)	11.9826(8)
b (Å)	16.222(3)	15.8905(11)
c (Å)	14.048(3)	14.0680(10)
α (°)	90	90
β (°)	90.000(3)	94.917(2)
γ (°)	90	90
Volume (A^3)	2575.3(9)	2668.8(3)
Z, D_{calc} ($Mg\,m^{-3}$)	4, 1.527	4, 1.533
Absorption coefficient (mm^{-1})	1.108	1.072
$F(000)$	1228	1276
Crystal size (mm)	$0.35 \times 0.30 \times 0.25$	$0.36 \times 0.26 \times 0.12$
θ range for data collection (°)	1.80–28.01	1.71–28.04
Limiting indices	$-14 \leqslant h \leqslant 14$, $-20 \leqslant k \leqslant 21$, $-18 \leqslant l \leqslant 10$	$-15 \leqslant h \leqslant 7$, $-20 \leqslant k \leqslant 20$, $-17 \leqslant l \leqslant 18$
Reflections collected/unique	15150/5917 ($R_{(int)} = 0.1077$)	14777/5966 ($R_{(int)} = 0.0466$)
Completeness to θ	28.01, 95.1%	28.04, 92.3%
Absorption correction	SADABS	SADABS
Maximum and minimum transmission	0.7692 and 0.6978	0.8821 and 0.6988
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5917/0/316	5966/0/334
Goodness-of-fit on F^2	0.966	0.836
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0867$, $wR_2 = 0.2242$	$R_1 = 0.0527$, $wR_2 = 0.1241$
R indices (all data)	$R_1 = 0.1223$, $wR_2 = 0.2445$	$R_1 = 0.1379$, $wR_2 = 0.1438$
Largest difference peak and hole ($e\,A^{-3}$)	1.790 and −1.241	0.589 and −0.445

Table 2
Selected bond lengths (Å) and angles (°) for [Cu(PMDT)(bipy)]$(ClO_4)_2$

Cu(1)–N(10)	2.021(4)	Cu(1)–N(12)	2.106(4)
Cu(1)–N(21)	2.022(4)	Cu(1)–N(22)	2.232(4)
Cu(1)–N(11)	2.094(4)		
N(10)–Cu(1)–N(21)	167.80(18)	N(11)–Cu(1)–N(12)	159.3(2)
N(10)–Cu(1)–N(11)	84.59(18)	N(10)–Cu(1)–N(22)	114.27(17)
N(21)–Cu(1)–N(11)	93.00(17)	N(21)–Cu(1)–N(22)	77.90(17)
N(10)–Cu(1)–N(12)	84.24(18)	N(11)–Cu(1)–N(22)	98.75(17)
N(21)–Cu(1)–N(12)	94.25(18)	N(12)–Cu(1)–N(22)	101.7(2)

Table 3
Selected bond lengths (Å) and angles (°) for [Cu(PMDT)(phen)]-$(ClO_4)_2$

Cu(1)–N(21)	2.010(4)	Cu(1)–N(12)	2.097(4)
Cu(1)–N(10)	2.023(4)	Cu(1)–N(22)	2.247(3)
Cu(1)–N(11)	2.087(4)		
N(21)–Cu(1)–N(10)	167.16(15)	N(11)–Cu(1)–N(12)	160.36(16)
N(21)–Cu(1)–N(11)	93.43(15)	N(21)–Cu(1)–N(22)	78.62(15)
N(10)–Cu(1)–N(11)	84.79(16)	N(10)–Cu(1)–N(22)	114.20(15)
N(21)–Cu(1)–N(12)	92.64(16)	N(11)–Cu(1)–N(22)	101.75(15)
N(10)–Cu(1)–N(12)	85.15(17)	N(12)–Cu(1)–N(22)	97.76(14)

(phen)]$(ClO_4)_2$ crystallizes in the monoclinic with the space group of $P2(1)/c$ (No. 14), $a = 11.9826(8)$ Å, $b = 15.8905(11)$ Å, $c = 14.0680(10)$ Å, $\alpha = 90°$, $\beta = 94.917(2)°$ and $\gamma = 90°$. The ORTEP diagram of the molecule with the atomic numbering is shown in Fig. 2. One tridentate ligand (PMDT) and one bidentate ligand (phen) are coordinated with the copper(II) center. The coordination sites in [Cu(PMDT)(phen)]$(ClO_4)_2$ are the

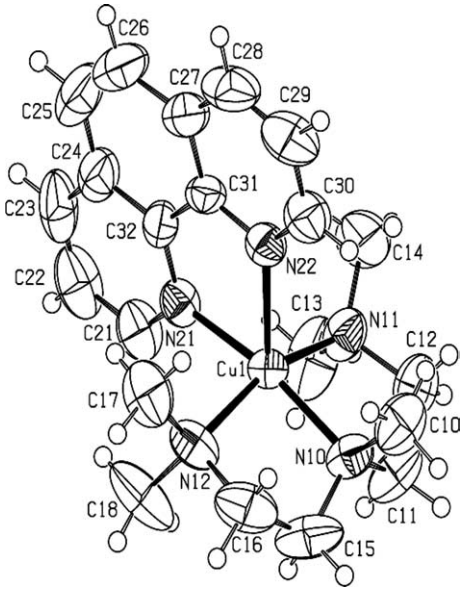

Fig. 2. ORTEP view for the complex cation of $[Cu(PMDT)(phen)]^{2+}$.

tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine group Cu–N(10) = 2.023(4) Å, Cu–N(11) = 2.087(4) Å and Cu–N(12) = 2.097(4) and hydrocyclic N of the phen Cu–N(21) = 2.010(4) Å and Cu–N(22) = 2.247(3) Å. Similarly, in [Cu(PMDT)(bipy)]$(ClO_4)_2$ the diethylenetriamine groups are Cu–N(10) = 2.021(4) Å, Cu–N(11) = 2.094(4) Å and Cu–N(12) = 2.106(4) Å and heterocyclic N of bipy Cu–N(21) = 2.0224(4) Å and Cu–N(22) = 2.232(4) Å. In the five-coordinate structures, the PMDT base occupies the basal plane. The phen ligand displays axial–equatorial coordination. Complex [Cu(PMDT)bipy]$(ClO_4)_2$ crystallizes in the monoclinic with the space group of $P2(1)/c$ (No. 14), $a = 11.301(2)$ Å, $b = 16.222(3)$ Å, $c = 14.048(3)$ Å, $\alpha = 90°$, $\beta = 90.000(3)°$ and $\gamma = 90°$. The ORTEP diagram of the molecule with the atomic numbering is also shown in Fig. 3. The coordination geometry in this complex is distorted square pyramidal (4 + 1). The NNN-donor atoms of PMDT occupy the basal plane. The NN-donor heterocyclic base displays axial-equatorial binding made. The distortion in the square pyramidal structure is mode in $[Cu(PMDT)(bipy)]^{2+}$ ($\tau = 0.061$) than in $[Cu(PMDT)(phen)]^{2+}$ ($\tau = 0.05$). Similar τ values [60] in the complexes [Cu(L)(bipy)] neutral complexes (L = ONS-donor thiosemicarbazones).

Both complexes show significant hydrogen bonding interactions. Relevant hydrogen bonding distances are given in Tables 4 and 5. Complexes [Cu(PMDT)(bipy)]-$(ClO_4)_2$ and [Cu(PMDT)(phen)]$(ClO_4)_2$ exhibit similar hydrogen bonding pattern built up from the N–H···O hydrogen bonds. A stereoscopic view of the packing of these two mixed ligand complexes is shown in Figs. 4 and 5. Hydrogen bonding occurs between hydrogen atoms of the coordinated PMDT molecule and oxygen

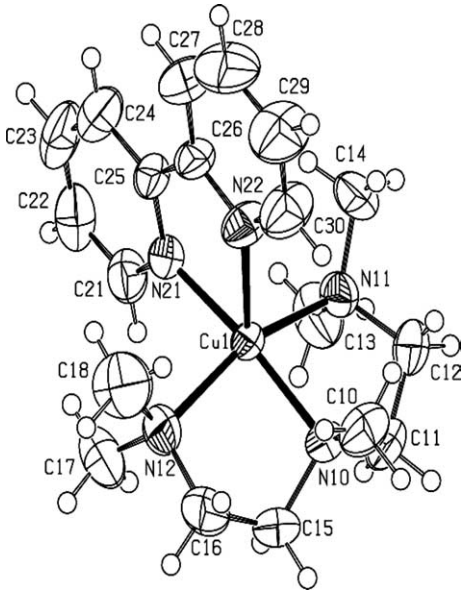

Fig. 3. ORTEP view for the complex cation of $[Cu(PMDT)(bipy)]^{2+}$.

Table 4
Hydrogen bonds for [Cu(PMDT)bipy]$(ClO_4)_2$ (Å and °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(10)–H(10C)···O(13)[a]	0.9600	2.5366	3.4911	172.78
C(13)–H(13C)···O(14)[b]	0.9600	2.5418	3.4216	152.40
C(16)–H(16A)···O(23)[c]	0.9700	2.5662	3.5052	162.96
C(16)–H(16B)···O(22)[d]	0.9700	2.5737	3.4016	143.36
C(21)–H(21)···O(11)[e]	0.9300	2.5787	3.3673	142.86
C(24)–H(24)···O(23)	0.9300	2.5471	3.3352	142.75
C(29)–H(29)···O(13)[f]	0.9300	2.5469	3.2018	127.75

Symmetry transformations used to generate equivalent atoms: [a] $-x, 1/2+y, 1/2-z$, [b] $1-x, 1/2+y, 1/2-z$, [c] $-1+x, y, z$, [d] $-1+x, 1/2-y, 1/2+z$, [e] $x, 1/2-y, 1/2+z$, [f] $x, 1/2-y, -1/2+z$.

Table 5
Hydrogen bonds for [Cu(PMDT)phen]$(ClO_4)_2$ (Å and °)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
C(10)–H(10B)···O(13)[a]	0.9600	2.4916	3.3453	148.11
C(12)–H(12B)···O(11)[b]	0.9700	2.5227	3.4736	166.61
C(25)–H(25)···O(11)[c]	0.9300	2.4870	3.2735	142.42

Symmetry transformations used to generate equivalent atoms: [a] $1-x, -1/2+y, 1/2-z$, [b] $x, 1/2-y, 1/2+z$, [c] $-1+x, 1/2-y, 1/2+z$.

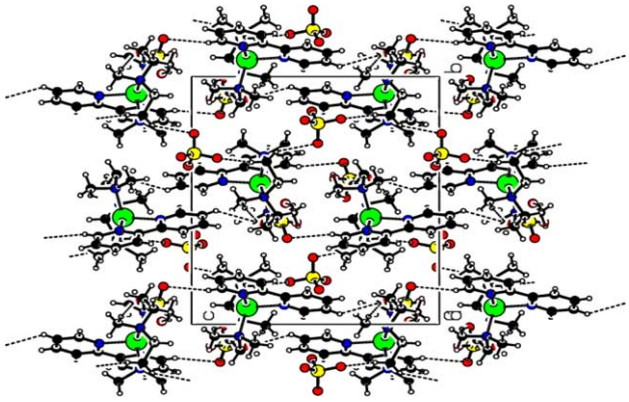

Fig. 4. Unit cell diagram of [Cu(PMDT)(bipy)]$(ClO_4)_2$.

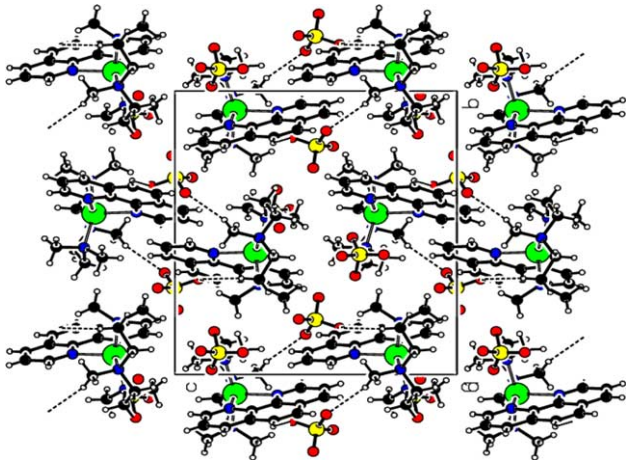

Fig. 5. Unit cell diagram of [Cu(PMDT)(phen)]$(ClO_4)_2$.

atoms of the perchlorate group, as shown by the dashed line in Figs. 4 and 5. The crystal packing of $[Cu(PMDT)(bipy)](ClO_4)_2$ is (Fig. 4) stabilized by a three dimensional hydrogen bonding network. The O···H contact ranges from 2.5366 to 2.5787 Å with mean C–H–O angle of 149.26°. The complex $[Cu(PMDT)(phen)](ClO_4)_2$ has minor impact on crystal packing (Fig. 5). The O···H contacts are as large as 2.5227 Å and the mean C–H···O angle being 152.38° reflecting the weakness of such intermolecular interactions in the solid state.

3.5. Biological activities

3.5.1. Antimicrobial activity

Both complexes were tested for antimicrobial activity. The susceptibility of certain strains of bacteria towards the present metal complexes was judged by measuring the size of inhibition diameter. Results of antimicrobial assessment of compounds are presented in Table 6. The growth inhibitory effects were observed against the following bacterial pathogens, *Pseudomonas pyocyanea*, *Staphylococcus aureus* and *Klebsiella acrogens*. It was noted that $[Cu(PMDT)(bipy)](ClO_4)_2$ was more effective against *P. Pyocyanea* and *Klebsiella* sp. than *S. aureus*, and later showed somewhat resistant property against $[Cu(PMDT)(bipy)](ClO_4)_2$. $[Cu(PMDT)(phen)](ClO_4)_2$ fall next to $[Cu(PMDT)bipy](ClO_4)_2$ because *K. acrogens* and *S. aureus* were more susceptible than *Pseudomonas* sp. The zone of inhibition differs significantly. Among fungal species three isolates were taken into consideration and were *Rhizopus* sp., *Aspergilles flavus* and *Fusarium* sp. The zones of inhibition of these compounds against those fungi were recorded in Table 6. Similar trends were observed as in the case of bacteria. It was noted that *Fusarium* sp. was highly susceptible against $[Cu(PMDT)(phen)](ClO_4)_2$. Another two fungi *Rhizopas* and *Aspergillus flavus* showed least effectiveness against $[Cu(PMDT)(bipy)](ClO_4)_2$ but comparatively more susceptible towards $[Cu(PMDT)(phen)](ClO_4)_2$ compound. Similar antimicrobial results were reported by Tarafder et al. [61] and also by our school [62] on simple copper(II) binary and ternary complexes.

Table 7
Superoxide dismutase activity of some copper(II) complexes

S. no.	Complex	Ic_{50} ($\mu mol\,dm^{-3}$)	Ref.
1.	$[Cu(PMDT)(OH_2)](ClO_4)_2$	149	[37]
2.	$[Cu(PMDT)(ImH)](ClO_4)_2$	125	[37]
3.	$[Cu(glygly)]\cdot 3H_2O$	132	[46]
4.	$[Cu(glygly)(bipy)]\cdot 3H_2O$	22	[46]
5.	$[Cu(glygly)(phen)]\cdot 3H_2O$	26	[46]
6.	$[Cu(PMDT)(bipy)](ClO_4)_2$	105	This work
7.	$[Cu(PMDT)(phen)](ClO_4)_2$	111	This work

glygly, glycylglycine; PMDT, pentamethyldiethylenetriamine.

3.5.2. Superoxide dismutase activity

The superoxide dismutase activity data for both complexes have been compiled in Table 7 along with activity data of some more similar complexes [37,46]. The data suggest that the square pyramidal $[(Cu(PMDT)(phen)](ClO_4)_2$ show moderate activity. In the present complexes, axial and remaining equatorial position occupied by either 2,2′-bipyridine or 1,10-phenanthroline causes enhancement of SOD activity. The higher SOD activity is due to the presence of α-diimine ligands (bipy or phen). A greater interaction between superoxide ion and Cu(II) in mixed ligand complex is induced due to the stronger axial bond [63] which results in an increased catalytic activity. In addition, α-diimine ligands stabilize the Cu(I) complex formed during superoxide dismutation reaction which further reacts with superoxide ion to give hydrogen peroxide. The distorted geometry of these complexes may favor the geometrical change, which is essential for the catalysis as the geometry of copper in the SOD enzyme also changes from distorted square pyramidal [64,65].

4. Conclusions

Two mixed ligand complexes having tridentate polyamine and polypyridine ligands are prepared and

Table 6
Antimicrobial activity of $[Cu(PMDT)(bipy)](ClO_4)_2$ and $[Cu(PMDT)(phen)](ClO_4)_2$ against human pathogens

S. no.	Test organisms	Zone of inhibition (nm)	
		$[Cu(PMDT)(bipy)](ClO_4)_2$	$[Cu(PMDT)(phen)](ClO_4)_2$
	Bacterial species		
1.	*Pseudomonas pyocyanea*	10.5	7.5
2.	*K. acrogens*	8.3	12.6
3.	*S. aureus*	R	15.5
	Fungal species		
4.	*Fusarium* sp.	14.2	6.5
5.	*Rhizopus* sp.	6.5	10.5
6.	*Aspergillus flavus*	7.2	12.6

R, Resistant.

structurally characterized. These complexes show extensive hydrogen bonding network involving the complex and perchlorate molecules. The spectral results are in agreement with the symmetry of the copper(II) derived from the X-ray structure determination. These compounds reveal their potent antimicrobial effect.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge crystallographic Data Centre, CCDC No. 214736 for complex [Cu(PMDT)(phen)]$(ClO_4)_2$ and CCDC No. 214737 for complex [Cu(PMDT)(bipy)]$(ClO_4)_2$. Copies of this information be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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