

X-ray, spectral and biological (antimicrobial and superoxide dismutase) studies of oxalato bridged Cu^{II}–Ni^{II} and Cu^{II}–Zn^{II} complexes with pentamethyldiethylenetriamine as capping ligand

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Abstract

X-band electron spin resonance (ESR) and electronic spectra of oxalato bridged heterodinuclear Cu–Ni and Cu–Zn complexes, viz., [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN and [(PMDT)Cu–Ox–Zn(PMDT)](BPh₄)₂ · 2CH₃CN, where PMDT = pentamethyldiethylenetriamine, Ox = oxalate ion have been described. Complex [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN has been structurally characterized. This complex crystallizes in the monoclinic space group, C₂ (No. 5) with the unit parameters $a = 20.445(4)$ Å, $b = 14.884(3)$ Å, $c = 23.174(5)$ Å, $\alpha = 90^\circ$, $\beta = 102.693(4)^\circ$, $\gamma = 90^\circ$, $V = 6880(2)$ Å³ and $Z = 4$. The structure refined to $R = 0.0354$ and $R_w = 0.0853$ for 21,109 reflections with $I > 2\sigma(I)$ using 765 parameters, shows the presence of a MN₃O₂ chromophore in a distorted trigonal-bipyramidal (TBP) heterometallic complex with oxalate dianion. Taking with an equatorial Cu–O = 2.137(8) Å and an axial Cu–O = 1.961(6) Å coordination site at Cu(II) ion and equatorial Ni–O = 2.178(7) Å and axial Ni–O = 1.994(9) Å coordination site at Ni(II) ion. The Cu–Ni distance is 5.3532(9) Å and Cu–C₂O₄–Ni unit is planar. The [(PMDT)Cu–Ox–Ni(PMDT)]²⁺ shows the ESR spectrum of the antiferromagnetic spin exchange with each dinuclear delocalization of the unpaired electron over the unit and spin-doublet ground state which demonstrates the Cu–Ox–Ni core. Antimicrobial and superoxide dismutase (SOD) activities of these complexes have also been measured.

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1. Introduction

Synthetic dinuclear transition-metal complexes provide models for metalloprotein active sites and lend in-

sight toward the design of new catalysts. Dinuclear complexes are of extensive investigation owing to their biological and industrial application [1]. Hetero dinuclear complexes particularly those comprising of copper(II) and zinc(II) within the same ligand frame work are gaining momentum due to their mimicking behaviour with active centre of copper zinc superoxide dismutase [2–4]. Copper complexes have found possible medical uses in the treatment of many diseases including cancer [5,6]. It has been suggested that the anticancer activity of some copper(II) complexes may be based on their ability to inhibit DNA synthesis [5]. One further possible mechanism of action that has been studied for certain complexes involves the scavenging of superoxide

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anion [5]. Some metal complexes may be expected to be biologically active. The demand for new and better antibacterial is driven by (a) the problem of bacterial resistance and (b) the rate at which bacterial resistance develops and shifts acakrate. The most alarming aspect of this acceleration is the speed with which resistance has spread among Gram positive organisms (*Pneumococci*, *Enterococci* and *Staphylococci*). Many of them release relatively large amounts of β -lactamase into the surrounding medium and they can destroy the β -lactamic antibiotics by hydrolysis of the β -lactamring, this being the most prevalent mechanism of resistance [5,6].

Some oxalato-bridged [7–12] dinuclear complexes have been reported but these are homometallic. There is far less work published on heterodinuclear oxalato bridged complexes. Recently a single heterodinuclear oxalato bridged complex was reported by Yamada et al. [9].

Therefore, in the course of our studies on synthetic dinuclear transition-metal complexes [13–18], we have synthesized and characterized two heterodinuclear metal complexes [(PMDT)Cu–Ox–Zn(PMDT)](BPh₄)₂ · 2CH₃CN and [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN. Biological activities (antibacterial and superoxide dismutase) of these complexes have been studied. The crystal structure of [(PMDT)Cu–Ox–Ni (PMDT)](BPh₄)₂ · 2CH₃CN is also presented.

2. Experimental

2.1. Materials

Pentamethyldiethylenetriamine (Aldrich), sodium oxalate (s.d. fine chem.), copper perchlorate hexahydrate (Aldrich) were used as supplied. Other chemicals used were of reagent grade.

2.2. Synthesis

2.2.1. Synthesis of [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN

A aqueous solution of Cu(ClO₄)₂ · 6H₂O (0.005 mmol) and PMDT (0.015 mmol) and Na₂C₂O₄ (0.005 mmol) were mixed together and stirred well (solution A). Similarly aqueous solution of Ni(ClO₄)₂ · 6H₂O (0.005 mmol) and PMDT (0.015 mmol) were mixed and stirred well (solution B). Solutions A and B were mixed together and stirred well. Addition of aqueous solution of NaBPh₄ gave the desired dark blue product. The product was washed, recrystallized in CH₃CN solution and dried in vacuo at room temperature. Yield: 65%. This heterodinuclear complex gives satisfactory microanalysis: found: C, 66.93; H, 7.26; N, 8.65; Cu, 5.02 and Ni, 4.63. Calc.: C, 67.65; H, 7.20; N, 8.77; Cu, 4.97; Ni, 4.59%.

2.2.2. Synthesis of [(PMDT)Cu–Ox–Zn(PMDT)](BPh₄)₂ · 2CH₃CN

This was also synthesized by the above-described method. Zinc perchlorate hexahydrate was used as a source of zinc. This heterodinuclear complex gives satisfactory microanalysis: found: C, 67.00; H, 7.24; N, 8.88; Cu, 4.95; Zn, 5.12. Calc.: C, 67.28; H, 7.16; N, 8.72; Cu, 4.94; Zn, 5.09%.

2.3. Physical measurements

2.3.1. Magnetic moment

Magnetic susceptibility measurements were recorded on a Gouy balance at room temperature. Hg[Co(NCS)₄] cobaltate(II) was used as a calibrant (16.44×10^{-6} cgs unit).

2.3.2. FAB mass spectra

FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature (r.t.) with *m*-nitrobenzyl alcohol as the matrix.

2.3.3. ESR spectra

ESR spectra of the complexes were recorded on a Varian E-line Century Series Spectrometer with a dual cavity at X-band radiation using 100 kHz modulation frequency. The spectra were calibrated by using a sample of tetracyanoethylene (TCNE). Varian quartz tubes were employed for taking ESR spectra of powder and frozen solution.

2.3.4. Electronic spectra

The electronic spectra of the samples were run in CH₃CN and nujol on a Shimadzu UV–Vis 160 spectrophotometer.

2.3.5. Bio activity

SOD activity and antimicrobial (antibacterial) activities were evaluated using the following methods.

2.3.6. SOD activity

In vitro SOD activity was measured using alkaline dimethyl sulphoxide (DMSO) as a source of superoxide radical (O₂⁻) and nitrobluetetrazolium (NBT) as scavenger [19,20].

2.3.7. Antimicrobial activity measurement

The in vitro antimicrobial (antibacterial) activities of these complexes were tested using paper disc diffusion method [21]. The chosen strains were G(+) *Staphylococcus* and G(-) *Proteus vulgaris*, *Salmonella*, *Pseudomonas* sp. and *Escherichia coli*. The liquid medium containing the bacterial subcultures was autoclaved for 20 min at 121 °C and at 15 lb pressure before inocula-

tion. The bacteria were then cultured for 24 h at 36 °C in an incubator. Nutrient agar was poured in to 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 centre 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.

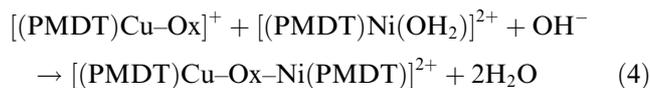
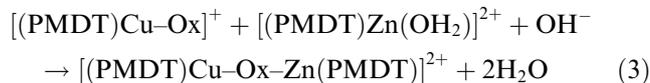
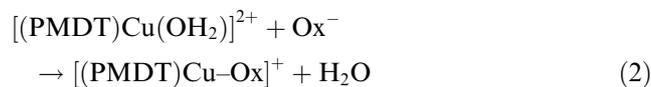
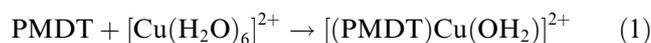
2.3.8. Crystal structure determination

A blue prismatic crystal of [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN 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 K α radiation ($\lambda = 0.71073$ Å) was used throughout. The data were processed with SAINT [22] and corrected for absorption using SADABS (transmission factors: 1.000–0.663) [23]. The structure was solved by direct methods using the program SHELXS-97 [24] and refined by full-matrix least-squares techniques against F^2 using SHELXL-97 [25]. Positional and anisotropic atomic displacement parameters were refined for all nonhydrogen atoms except for the C and N atoms of two acetonitrile molecules (refined isotropically). Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Isotropic atomic displacement parameters for hydrogen atoms were constrained to be 1.2 (1.5 for methyl groups). The Flack X parameter (absolute structure parameter) was calculated to be 0.00(5) for the present structure and 0.99(5) for the inverted structure, thus providing strong evidence that the absolute structure has been assigned correctly [26]. 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. Atomic scattering factors from “International Tables for Crystallography” [27], molecular graphics from PLATON [28] and SCHAKAL [29].

3. Results and discussion

3.1. Synthesis and molecular structure

By the following sequential routes the oxalato bridged complexes have been synthesized:



All the above-synthesized complexes gave satisfactory elemental analysis. The FAB mass spectra of the dinuclear complexes show the base peak at m/z 557 (M^+). The FAB mass spectra thus confirm the authenticity of the complexes. The crystal structure of the complex [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN consists of a discrete [(PMDT)Cu–Ox–Ni(PMDT)]²⁺, (BPh₄)₂ and CH₃CN units. The structure of the centrosymmetric complex [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ needle form was determined by single crystal X-ray crystallographic techniques. The crystallographic and refinement data are given in Table 1 and bond angle and distances are presented in Table 2.

The oxalate bridged and first coordination sphere ligand atoms are labeled as indicated in Fig. 1. The Cu–Ni distance is 5.3532(9) Å. The local Cu(II) and Ni(II) environments and bridging group in the complex cation are given in Fig. 1. Each metal(II) ion and PMDT ligand forms two five membered chelate rings and apparently enforces a distorted TBP geometry. In two known complexes [Cu₂(Et₅dien)₂(C₂O₄)]²⁺ and Cu(Et₄dien)(N₃)Br the coordination is clearly trigonal bipyramidal [30] with the unique (secondary) nitrogen atom occupying one axial site. Also the crystallographic investigation of [Cu₂(Me₅dien)₂(N₃)₂](BPh₄)₂ and [Cu₂(Me₅dien)₂(CA)](BPh₄)₂, where CA is dianion, has shown that the copper coordination geometry is intermediate between trigonal bipyramidal (TBP) and square pyramidal (SP) [31]. The monomeric compounds [32,33] [Co(Me₅dien)]Cl₂ and [Co(Et₄dien)]Cl₂ also appear to adopt an intermediate geometry. Almost all the N bond angle fall within the range observed for Cu^{II}–dien complexes. Thus geometries of the present complex should be a SP–TBP intermediate.

The molecular dimensions of the oxalate group are relatively invariant in all Cu(II) oxalate complexes. The oxalate C–C bond of [Cu₂Et₅(dien)₂(C₂O₄)](BPh₄)₂ is 1.53(1) Å where as of the present complex it is 1.554(5) Å and is slightly greater than the reported homodinuclear complex. The O–C–O angle of the present complex 125.4(10) Å falls within the normal range for the oxalate dianion [34,35].

The BPh₄[−] anion has typical bond distances and angles. All the four-phenyl groups are planar. The mean B–C bond distance is 1.645 Å and mean C–C distance is 1.383 Å. The bond angle of the each phenyl group are found in the range of 113.2°–125.2° indicating the presence of some distortion. These results are in accord with the previous crystallographic work [36,37] on BPh₄[−]

Table 1

Crystal data and structure refinement for [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN

Empirical formula	C ₇₂ H ₉₂ B ₂ CuN ₈ NiO ₄
Formula weight	1277.41
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, C2 (No. 5)
Unit cell dimensions	
<i>a</i> (Å)	20.445(4)
<i>b</i> (Å)	14.884(3)
<i>c</i> (Å)	23.174(5)
α (°)	90
β (°)	102.693(4)
γ (°)	90
<i>V</i> (Å ³)	6880(2)
<i>Z</i> , calculated density (Mg/m ³)	4, 1.233
Absorption coefficient (mm ⁻¹)	0.636
<i>F</i> (000)	2716
Crystal size (mm)	0.69 × 0.50 × 0.24
θ range for data collection	0.90°–26.44°
Limiting indices	–24 ≤ <i>h</i> ≤ 25, 0 ≤ <i>k</i> ≤ 18, –28 ≤ <i>l</i> ≤ 0
Reflections collected/unique	21,109/7341 [<i>R</i> _{int} = 0.0427]
Completeness to θ = 26.44°	99.5%
Absorption correction	SADABS
Maximum and minimum transmission	0.8624 and 0.6681
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7341/1/765
Goodness-of-fit on <i>F</i> ²	1.044
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0354, <i>wR</i> ₂ = 0.0853
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0639, <i>wR</i> ₂ = 0.1039
Absolute structure parameter	0.00(5)
Largest difference peak and hole	0.273 and –0.368 e Å ⁻³

compounds, which also indicates some amount of crowding about Boron atom.

3.2. Magnetic moment

The room temperature magnetic moment values of these complexes are also measured. At room temperature the magnetic moment value (1.68 B.M.) of the compound [(PMDT)Cu–Ox–Ni(PMDT)]²⁺ is consider-

ably lower than spin only value for *S*_T = 1/2 resulting from the spin coupling between Cu=S = 1/2 and S=Ni = 1. This magnetic behaviour is quite characteristic of antiferromagnetic coupling between the paramagnetic nickel(II) and copper(II) centers. Similar magnetic behaviour is reported by Masami et al. [38] and also by our school [39]. The room temperature value (*μ*_{eff} = 1.91 B.M.) for [(PMDT)Cu–Ox–Zn(PMDT)]²⁺ is in agreement with one spin (*S* = 1/2) system.

Table 2

Selected bond lengths (Å) and angles (°) for [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN

Cu(1)–O(11)	1.961(6)	Ni(1)–O(22)	1.973(6)
Cu(1)–N(12)	2.036(7)	Ni(1)–N(23)	1.987(10)
Cu(1)–N(11)	2.050(8)	Ni(1)–N(22)	1.994(9)
Cu(1)–N(13)	2.075(10)	Ni(1)–N(21)	2.042(9)
Cu(1)–O(21)	2.137(8)	Ni(1)–O(12)	2.178(7)
Cu(1)–Ni(1)	5.3532(9)		
O(11)–Cu(1)–N(12)	177.2(4)	O(22)–Ni(1)–N(23)	93.6(3)
O(11)–Cu(1)–N(11)	93.5(3)	O(22)–Ni(1)–N(22)	177.8(4)
N(12)–Cu(1)–N(11)	87.2(3)	N(23)–Ni(1)–N(22)	86.2(4)
O(11)–Cu(1)–N(13)	92.3(3)	O(22)–Ni(1)–N(21)	92.6(3)
N(12)–Cu(1)–N(13)	85.6(4)	N(23)–Ni(1)–N(21)	146.9(4)
N(11)–Cu(1)–N(13)	145.3(4)	N(22)–Ni(1)–N(21)	86.4(4)
O(11)–Cu(1)–O(21)	81.7(3)	O(22)–Ni(1)–O(12)	80.7(3)
N(12)–Cu(1)–O(21)	100.8(3)	N(23)–Ni(1)–O(12)	109.4(4)
N(11)–Cu(1)–O(21)	106.2(4)	N(22)–Ni(1)–O(12)	101.5(3)
N(13)–Cu(1)–O(21)	108.5(4)	N(21)–Ni(1)–O(12)	103.7(4)

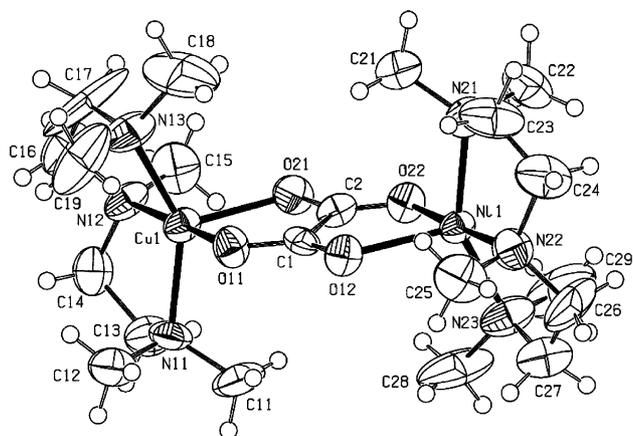


Fig. 1. ORTEP diagram of $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})]^{2+}$.

3.3. ESR studies

X-band ESR spectra of the complexes were recorded in polycrystalline state and also in 100% DMSO solution at room temperature and at liquid nitrogen temperature (77 K). The ESR spectra are shown in Fig. 2. The polycrystalline ESR spectra of complex $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Zn}(\text{PMDT})]^{2+}$ shows a weak half field signal ($\Delta M_s = 2$) at room temperature and at liquid nitrogen temperature. At both temperatures the spectral features are same only better resolution was obtained here. These types of signals were observed in other known complexes [39] and has been attributed to intermolecular spin-spin interaction arising due to solid effect. In case of $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})]^{2+}$ four clear intense features in the low field region were ob-

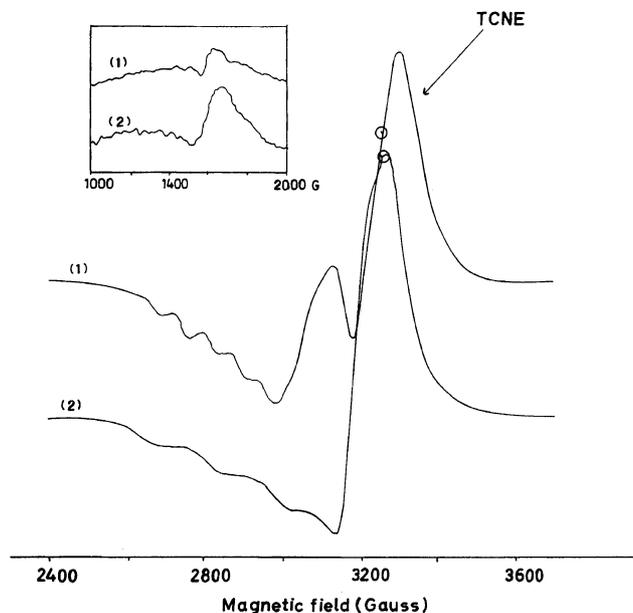


Fig. 2. Polycrystalline ESR spectra of (1) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ and (2) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Zn}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$.

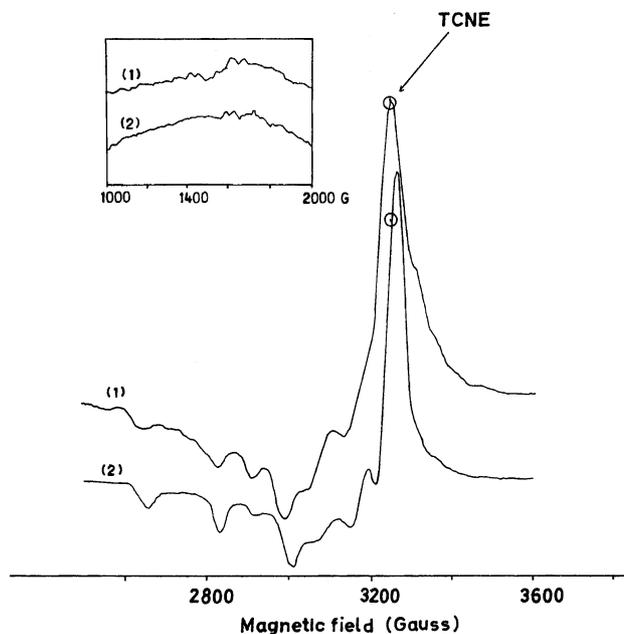


Fig. 3. ESR spectra in 100% DMSO of (1) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ and (2) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Zn}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$.

served. Similar lines again results in 100% DMSO at liquid nitrogen temperature (Fig. 3). The four hyper fine lines in spin coupled $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ are easy to understand, as only Cu has isotopes ^{63}Cu (69.1%) and ^{65}Cu (30.9%) with $I_{\text{Cu}} = 3/2$, whereas Ni has isotopes ^{61}Ni with $I_{\text{Ni}} = 3/2$, but its natural abundance is very low, 1.25%. Thus the hyperfine lines due to the copper nucleus is observed for exchange-coupled $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$. The hyperfine coupling constant ($A_{\text{Cu}} = 75$ G) calculated for this complex is related to the hyperfine coupling constant A_{Cu} for a mononuclear copper(II) complex by the expression $A_{\text{Cu}} = -A_{\text{Cu}}/3$. The hyperfine coupling constant for $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Zn}(\text{PMDT})]^{2+}$ is (175 G). The value of coupling constant A_{Cu} for $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})]^{2+}$ (75 G) is indeed one third for

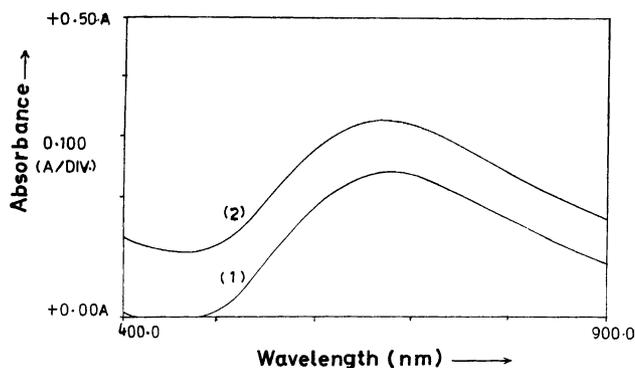


Fig. 4. UV-Vis spectra in 100% DMSO of (1) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Ni}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ and (2) $[(\text{PMDT})\text{Cu}-\text{Ox}-\text{Zn}(\text{PMDT})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$.

Table 3
SOD and antimicrobial activity of copper(II) complexes

S.No.	Complex	Ic ₅₀ (μM)	Diameter of inhibition zone				
			<i>Pseudomonas pyocyanea</i>	<i>Salmonella typhineurium</i>	<i>Staphylococcus albus</i>	<i>E. coli</i>	<i>Proteus vulgaris</i>
1	[(PMDT)Cu–Ox–Zn(PMDT)]-(BPh ₄) ₂ · 2CH ₃ CN	205	10.0	10.6	R	R	R
2	[(PMDT)Cu–Ox–Ni(PMDT)]-(BPh ₄) ₂ · 2CH ₃ CN	216	3.0	12.0	10.6	2.8	R

R, resistant.

mononuclear d⁹ copper(II) systems [40], therefore confirms the binuclear nature in solid. The ESR spectra of these complexes in frozen solution, water/DMSO (1:1, v:v) exhibit the usual line shape for mononuclear copper(II) complexes with $g_{\parallel} > g_{\perp} > 2.03$ indicating the axial symmetry. The measured value of g_{\parallel} and g_{\perp} for the complexes Cu–Ox–Zn is 2.244 and 2.057. It should be pointed out that these values are quite close to that of Cu₂Zn₂SOD ($g_{\parallel} = 2.271$, $g_{\perp} = 2.083$) [41].

3.4. UV–Vis study

Electronic spectra of heterobinuclear oxalato bridged complexes are recorded in acetonitrile solution (Fig. 4). Both compounds gave similar features. Similarity in spectra is due to same kind of chemical environment in both the complexes. Both complexes show the λ_{\max} at 675 ± 5 nm and is assigned to a superposed band of d–d transition of Cu^{II} ion. Lack of absorption band at ~820 nm which is characteristic of trigonal pyramidal geometry [42] of copper(II) mononuclear systems implies that in solution no longer oxalato bridged survives. The observed bands are due to tetragonal near to square planar geometry. These results are similar to that of ESR work in frozen solution.

3.5. Antimicrobial activity of compounds against pathogens

The susceptibility of the 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 3. It was noted that antimicrobial activity of [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN was fairly good against *Salmonella* and *Staphylococcus* bacteria but against *P. pyocyanea* and *E. coli* its activity was very less. *Proteus* sp. was resistant against the present metal complexes. *Pseudomonas* sp. and *Salmonella* sp. were effective against [(PMDT)Cu–Ox–Ni(PMDT)]-(BPh₄)₂ · 2CH₃CN and [(PMDT)Cu–Ox–Zn(PMDT)]-(BPh₄)₂ · 2CH₃CN. Thus these complexes showed positive results against pathogens. But [(PMDT)Cu–Ox–Zn(PMDT)](BPh₄)₂ · 2CH₃CN was highly effective against

Pseudomonas sp., which is highly useful bacterium. Also [(PMDT)Cu–Ox–Ni(PMDT)](BPh₄)₂ · 2CH₃CN and [(PMDT)Cu–Ox–Zn(PMDT)](BPh₄)₂ · 2CH₃CN complexes were significantly positive and check the growth of *Salmonella typhi* which is a causative agent of pneumonia.

3.6. Superoxide dismutase activity

The superoxide dismutase activity of these complexes were also studied and are given in Table 3. These compound show less SOD activity (higher Ic₅₀) than the simple mononuclear complex [20]. Since oxalato bridged complexes show higher ligand field than the mononuclear complexes comprising of the same ligand. A strong ligand may oppose the interaction of the copper with superoxide radicals, being unfavourable to the probable formation of intermediate copper superoxide adduct [43].

In conclusion, our complexes appears to be a fairly good model for copper(II) site of intact Cu₂Zn₂SOD because it exhibits several structural and spectroscopic features similar to the active site of the enzyme.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge crystallographic Data Centre, CCDC No. 209270. Copies of this information be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB 2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc-cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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