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Copper(II) complexes of tridentate N,N,N',N''-pentamethyldiethylenetriamine: Superoxide dismutase and inhibitory activity against bacteria and fungi

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Abstract

A series of ternary copper(II) complexes containing same coordination sphere but difference in the counter ions, viz., $[Cu(PMDT)(OAc)]PF_6$ (1); $[Cu(PMDT)(OAc)]ClO_4$ (2); $[Cu(PMDT)(OAc)]BF_4$ (3) and $[Cu(PMDT)(OAc)]BPh_4$ (4) where PMDT = N, N, N', N'', pentamethyldiethylenetriamine, OAc = Acetate ion were synthesized and characterized by means of spectroscopic, magnetic and cyclic voltammetric measurements. In frozen solution e.p.r. spectra, an interesting relation $g_{||} > g_{\perp}$ has been observed which is a typical of the axially symmetric d⁹ Cu^{II} ($S_{Cu} = 1/2$) having an unpaired electron in a $d_{x^2-y^2}$ orbital. Single crystal X-ray analysis of (1) has revealed the presence of distorted square planar geometry. The influence of the counter ion on the complexes has been examined by performing some biological experiments like superoxide dismutase and anti-microbial activity.

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Keywords: Copper(II) complexes; Electron paramagnetic resonance (e.p.r.); Superoxide dismutase (SOD); Crystal structure; Anti-microbial activity

1. Introduction

Copper is a bioessential element with relevant oxidation states +1 and +2 and its coordination geometries are square planar or square pyramidal. Tridentate ligands have been extensively used in coordination chemistry in recent years [1]. Beside other reasons, the interest in these systems are concerned to the possibility of obtaining low symmetry four, five or six coordinated complexes, especially if significant steric ligand restrictions are present [2,3]. The presence of unsymmetrical metal environments in several biological systems (e.g. in copper enzymes) has been linked to their redox properties [4,5].

In our previous communications [6,7], we have reported a series of copper(II) complexes having diethylenetriamine and N,N,N',N'',N''-pentamethyldiethylenetriamine as tridentate ligands and some bidentate (2,2'-bipyridine, 1,10-phenanthroline) ligands. The N,N,N',N'',N''-pentamethyldiethylenetriamine

1386-1425/\$ – see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2006.04.017 (PMDT) is a potentially tridentate ligand capable of bonding through two amino groups and one imino group. Our interest in these complexes was associated with the structural, magnetic, spectroscopic and redox properties as well as catalytic (superoxide dismutase activity) and inhibitory activity against bacteria and fungi of [(PMDT)Cu(II)(OAc)]⁺ chelates bearing different anions. In this communication, we report the synthesis, characterization and biological activity of some Cu(II) complexes containing same coordination sphere but different in counter ions.

2. Experimental

2.1. Materials and methods

N,N,N',N'',N''-pentamethyldiethylenetriamine, NaPF₆, NaClO₄, NH₄BF₄ (Aldrich), copper(II) acetate monohydrate, NaBPh₄ (s.d. fine Chemicals) were used as purchased. Elemental analyses were performed on elemental analyzer. FAB mass spectra were recorded on a JEOL SX 102/DA 6000 mass

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spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The magnetic susceptibility data were recorded on a Gouy balance at room temperature using mercury(II) tetrathiocyanato cobaltate(II) ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. unit) as calibrant. e.p.r. spectra were recorded at RT and LNT (77 K) on a Varian E-line Century Series e.p.r. Spectrometer operating at 9.4 GHz with TCNE as a calibrant. UV-vis spectra were recorded on a Shimadzu UV-vis 160 spectrophotometer with quartz cells. The SOD activities were evaluated using alkaline DMSO as a source of superoxide radicals (O_2^-) and nitro blue tetrazolium (NBT) as scavanger [8,9]. The in vitro anti-microbial (antibacterial and antifungal) activities of these complexes were tested using paper disc diffusion method and agar plate technique [10,11]. A BAS-100 Epsilon electrochemical analyzer was used for cyclic voltammetric experiment on DMSO solution of the complex containing tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The three-electrode measurement was carried out at 298 K under nitrogen atmosphere with a platinum working electrode, a platinum wire auxiliary electrode and a silver/silver chloride reference electrode (Ag/AgCl).

2.2. Synthesis of the complexes

2.2.1. Preparation of [Cu(PMDT)(OAc)]PF₆ (1); [Cu(PMDT)(OAc)]ClO₄ (2); [Cu(PMDT)(OAc)]BF₄ (3) and [Cu(PMDT)(OAc)]BPh₄ (4)

All the present complexes were prepared by a general method. To an aqueous methanolic solution (15 ml 1:3, v/v) of copper acetate monohydrate (1 mmol, 0.199 g) a methanolic solution (10 ml) of PMDT (1 mmol, 0.137 g) was reacted under stirring for 0.5 h at 25 °C. After completion of the reaction, a saturated methanolic solution (5 ml) of NaPF₆ was added to the above reaction mixture and left for slow evaporation. After 3–4 days dark blue crystals of complex (1) were obtained. They were washed with diethyl ether and dried on air at room temperature, Yield 80%. Anal. Found: C, 30.00; H, 5.85; N, 9.52%. Calc. for $C_{11}H_{26}N_3CuO_2PF_6$: C, 29.94; H, 5.89; N, 9.52%. FAB Ms; *m/z* obs. (cal.) 295 (295.84).

Complexes (2), (3) and (4) were prepared as described above by employing NaClO₄, NH₄BF₄ and NaBPh₄, respectively in place of NaPF₆. Anal. Found: C, 33.75; H, 7.01; N, 10.55%. Calc. for C₁₁H₂₆N₃CuO₆Cl (2): C, 33.43; H, 6.58; N, 10.63%. FAB Ms; m/z obs. (cal.) 295 (295.84). Anal. Found: C, 34.60; H, 6.90; N, 11.02%. Calc. for C₁₁H₂₆N₃CuO₂BF₄ (3): C, 34.47; H, 6.79; N, 10.97%. FAB Ms; m/z obs. (cal.) 295 (295.84). Anal. Found: C, 21.45; H, 4.60; N, 7.11%. Calc. for C₃₅H₄₆N₃CuO₂B (4): C, 21.46; H, 4.22; N, 6.82%. FAB Ms; m/z obs. (cal.) 295 (295.84).

3. Results and discussion

3.1. Crystal structure

The crystal structure of the mononuclear copper(II) complex consists of cationic unit of $[Cu(PMDT)(OAc)]^+$ and un-coordinated one hexafluorophate ion. A perspective view of $[Cu(PMDT)(OAc)]PF_6$ (1) is shown in Fig. 1. Sum-



Fig. 1. ORTEP diagram of the complex [Cu(PMDT)(OAc)]PF6.

mary of crystal data and structure refinement parameters for [Cu(PMDT)(OAc)]⁺ are given in Table 1. Selected bond angle and bond distances are listed in Table 2. In this complex, PMDT is coordinated to copper(II) through two amino and one imino nitrogen and one oxygen (hydroxyl) from the acetate. The copper center in the complex has a distorted square planar environment.

Bond angles show that the coordination geometry around the copper atom is a distorted square planar, were N(3)Cu(1)N(2)

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Crystal data and structure refinement for	[(PMDT)Cu(OAc)](PF) ₆ (1
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Empirical formula	C ₁₁ H ₂₆ CuF ₆ N ₃ O ₂ P
Formula weight	440.86
Temperature (K)	293 (2)
Wavelength (Å)	0.70930
Crystal system	Monoclinic
Space group	P21
Unit cell dimensions	
<i>a</i> (Å)	6.4310 (7)
<i>b</i> (Å)	17.7140(10)
c (Å)	7.9960(5)
α (°)	90
β (°)	92.082 (7)
γ (°)	90
Volume (Å ³)	910.29 (13)
Z, calculated density (mg/m^3)	2, 1.608
Absorption coefficient (mm ⁻¹)	1.355
F (000)	454
Crystal size (mm)	$0.40 \times 0.35 \times 0.35$
θ range for data collection	2.29°-24.94°
Index ranges	$0 \le h \le 7, -21 \le k \le 0, -9 \le l \le 9$
Reflections collected/unique	$1802/1652 [R_{int} = 0.0581]$
Completeness to $2\theta = 24.94^{\circ}$	99.6%
Absorption correction	Ψ -scan
Max. and min. transmission	0.6485 and 0.6133
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1652/1/223
Goodness-of-fit on F^2	1.022
Final <i>R</i> indices $[I > 2\sigma (I)]$	$R_1 = 0.0372, wR_2 = 0.0889$
<i>R</i> indices (all data)	$R_1 = 0.0650, wR_2 = 0.0986$
Absolute structure parameter	-0.02 (5)
Largest diff. peak and hole $(e, Å^{-3})$	0.484 and -0.490

Table 2
Selected bond lengths (Å) and angles ($^{\circ}$) for [(PMDT)Cu(OAc)](PF) ₆ (1)

Cu(1)-O(2)	1.940(3)
Cu(1)-N(3)	1.990(13)
Cu(1)-N(2)	1.993(4)
Cu(1)-N(1)	2.117(12)
N(1)-C(3)	1.458(19)
N(1)-C(1)	1.47(2)
N(1)-C(2)	1.575(18)
N(2)-C(4)	1.476(19)
N(2)-C(5)	1.488(7)
N(2)-C(6)	1.49(2)
N(3)-C(9)	1.410(19)
N(3)-C(7)	1.49(2)
N(3)-C(8)	1.49(2)
O(2)-Cu(1)-N(3)	91.8(5)
O(2)-Cu(1)-N(2)	178.9(5)
N(3)-Cu(1)-N(2)	88.8(6)
O(2)-Cu(1)-N(1)	95.2(5)
N(3)-Cu(1)-N(1)	162.6(2)
N(2)-Cu(1)-N(1)	84.0(6)
C(3) - N(1) - Cu(1)	107.2(9)
C(1) - N(1) - Cu(1)	105.9(10)
C(2) - N(1) - Cu(1)	108.9(9)
C(4) - N(2) - Cu(1)	106.9(8)
C(5)-N(2)-Cu(1)	109.5(4)
C(6) - N(2) - Cu(1)	104.9(9)
C(9) - N(3) - Cu(1)	120.0(10)
C(7) - N(3) - Cu(1)	107.6(9)
C(8)-N(3)-Cu(1)	106.1(9)

is 88.8(6); N(3)Cu(1)N(1) and O(2)Cu(1)N(2) angles are 162.6(2) and 178.9(5), respectively. Above observation is in agreement with other four coordinated copper(II) systems [12]. Cu–O and Cu–N bond lengths are 1.940(3) and 1.990(13)–2.117(12), respectively and are in general agreement with similar complexes [6,7,13]. The elongation of the Cu–N bonds in the present complex with comparison to Cu–N bonds (1.990(13)–2.117(12)) containing diethylenetriamine (Cu–N 2.005(4)–2.186(4)) [7] clearly indicates the strong electron-withdrawing effect of the methyl substituents. All distances and angles in PF_6^- anion appear normal.

A stereoscopic view of the unit cell can be seen in Fig. 2 and this shows how the large PF_6^- ion isolate the $[Cu(PMDT)(OAc)]^+$ cation.



Fig. 2. Unit cell diagram of the complex [Cu(PMDT)(OAc)]PF₆.

3.2. Magnetic moment

The magnetic susceptibility measurements in the polycrystalline state show that the complexes are paramagnetic at ambient temperature. The observed magnetic moment values of the present complexes are quiet close to the values expected for copper(II) complexes without interaction. The magnetic moment values of the complexes are with in the range of 1.80–1.82 B.M. In case of complex (4) the value is found to be 1.78 B.M. This low value is due to magnetic interaction between two copper metal centres (intermolecular). Such type of magnetic interaction has been proved by our e.p.r. observations of the same complex. The magnetic moment value ($\mu_{eff.}$) for remaining complexes as indicated above lie within the range normally found for other copper(II) complexes [14,15].

3.3. e.p.r. Spectra

e.p.r. Spectra of the present complexes were recorded in polycrystalline and in glassy state at room temperature (r.t.) and liquid nitrogen temperature (l.n.t.), respectively. Derived e.p.r. spectral parameters are given in Table 3. Representative e.p.r. spectra are shown in Figs. 3 and 4. Polycrystalline spectra of the present complexes show a single broad line at room temperatures. The basic spectral features at both temperatures are same with slight better resolution at l.n.t. These broad line e.p.r. spectra are due to $\Delta Ms = \pm 1$ at $g = \sim 2.08$. $\Delta Ms = \pm$ signal (half-field signal) is observed in (4) only which is characteristic of a magnetic triplet [16,17]. However, when dissolved in coordinating solvents such as dimethyl sulphoxide, the samples provided a four line spectra typical of monomeric copper(II) species. The frozen solution e.p.r. spectra of these complexes in DMSO shows $g_{||} > g_{\perp}$. It is interesting that the relation $g_{||} > g_{\perp}$ is typical of the axially symmetric $d^9 \text{ Cu}^{\text{II}}$ ($S_{\text{Cu}} = 1/2$) having one unpaired electron in a $d_{x^2-y^2}$ orbital [18]. The spectra showed well resolved e.p.r. features arising out of $M_{\rm I} = +3/2$ component of copper giving a $A_{||}$ value 175 ± 1 G. No nitrogen



Fig. 3. e.p.r. Spectrum (liquid nitrogen temperature) in 100% DMSO of [Cu(PMDT)(OAc)]ClO₄.

.p.i. I arameters of copper(II) comp	ICACS					
Complexes	$g_{ }$	g_\perp	A (G)	g_1	<i>g</i> ₂	f(cm ⁻
Cu(PMDT)(OAc)]PF ₆ (1)	2.20	2.046	176	2.053	2.031	134
$Cu(PMDT)(OAc)]ClO_4$ (2)	2.20	2.042	174	2.148	2.074	135
Cu(PMDT)(OAc)]BF ₄ (3)	2.20	2.046	178	2.148	2.076	132
Cu(PMDT)(OAc)]BPh ₄ (4)	2.20	2.046	177	_	_	133

 Table 3

 e.p.r. Parameters of copper(II) complexes

superhyperfine splitting have been observed. The spectral features are similar to those reported for copper(II) – polyamines complexes[19,20].

The $g_{||}$ and $A_{||}$ values of the complexes are found to be almost the same, which indicate that the bonding is dominated by the PMDT moiety. The empirical factor $f = g_{||}/A_{||} \text{ cm}^{-1}$ is an index of tetragonal distortion and its value may vary from 105 to 135 for small to extreme distortion in square planar complexes and depends on the nature of the coordinated atoms [21]. The *f* values of the complexes are found to be in the range 132–135, indicating significant distortion from planarity.

As follows 135 (2) > 134 (1) > 133 (4) > 132 (3).

The above spectral observations are in agreement with X-ray diffraction studies for the complex [Cu(PMDT)(OAc)](PF₆).

3.4. UV-vis spectra

The UV-vis spectra of the present complexes were recorded in 100% DMSO. The visible spectra of the present complexes in solutions show that the absorption bands occurs at 650 ± 1 nm (Fig. 5), characteristic of a copper(II) $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ (²B_{1g} \rightarrow E_g) [22,23] transition in a tetragonal ligand field, in which the copper(II) has a distorted square planar geometry environment. The above observations are in agreement with those found from the X-ray data.



Fig. 4. Polycrystalline e.p.r. spectrum (room temperature) of (a) $[Cu(PMDT)(OAc)]PF_6$, (b) $[Cu(PMDT)(OAc)]ClO_4$ and (c) $[Cu(PMDT)(OAc)]BPh_4$.



Fig. 5. The UV–vis spectra $(0.003 \text{ mol}^{-1} \text{ dm}^{-3})$ of complexes (1) [Cu(PMDT)(OAc)]PF₆, (2) [Cu(PMDT)(OAc)]ClO₄, (3) [Cu(PMDT)(OAc)] BF₄ and (4) [Cu(PMDT)(OAc)]BPh₄.

3.5. Cyclic voltammetry

The redox behaviour of the present complexes has been examined by cyclic voltammetry (CV) under nitrogen atmosphere in dimethylsulphoxide, in the potential range +0.9 V to -0.8 V versus Ag/AgCl. Cyclic voltammetric data for the copper(II) complexes in 0.1 M TBAP-DMSO solution are listed in Table 4. The complexes show two quasireversible redox waves (Fig. 6) of an one-electron transfer corresponding to Cu(II)/Cu(I) and Cu(I)/Cu(0) redox couples. Complex (2) and (3) exhibit ill-defined anodic waves.

3.6. Biological activities

3.6.1. Anti-microbial activity

All complexes were tested for anti-microbial activity. The activity of the complexes were evaluated against different species of bacteria and fungi [11,24–26]. The susceptibility of the certain strains of bacteria and fungi towards the present metal complexes were judged by measuring the size of inhibition diameter.

In the present experiment, we have tested all the four complexes (1), (2), (3), and (4) against five bacterial cultures and four fungal cultures. These complexes showed significant

Table 4		
Cyclic voltammetric	data of copper(II)	complexes

Complex	Cu^{II}/I couple $E_{pa}(E_{pc}), V$	$Cu^{I/0}$ couple $E_{pa}(E_{pc}), V$
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	0.212(-0.380) (-0.208) (-0.223) 0.191(-0.216)	$\begin{array}{c} -0.215(-0.532) \\ (-0.322) \\ (0.293) \\ -0.142(-0.365) \end{array}$

Table 5
Anti-microbial activity of the title complexes against human pathogens

S. No.	Test organisms	Zone of inhibition (nm)				
		Complex (1)	Complex (2)	Complex (3)	Complex (4)	
Bacterial spec	ties					
1	Proteus vulgaris	2.1	3.5	R	1.0	
2	Streptococus sp.	2.6	4.9	R	3.5	
3	E. coli	R	2.6	3.6	R	
4	Pseudomonas pyocyanea	3.5	1.9	2.8	2.6	
5	Salmonella sp.	R	2.1	1.9	3.9	
Fungal specie	S					
6	Aspergillas nigar	6.5	6.3	R	5.8	
7	Alternaria	7.1	4.1	R	3.6	
8	Penicillium sp.	R	2.1	3.6	R	
9	Fusarium sp.	8.7	6.5	2.5	6.0	

R: resistant.

activity against Aspergillas vigan, Alterneria altemata, Penicillium sp. and Fusarium sp. a plant pathogen. It was noticed that complex (1) was the best antifungal agent in comparison to others. Showed least activity in comparison to other complexes. It was observed that bacterial species were more susceptible than fungi. Complex (2) was comparatively more effective than (1), (3) and (4) against all tested bacteria, but (3) was not effective against *P. vulgaris* and *Streptococcus* bacteria. This also showed least effectiveness against *Salmonella sp.* Complex (1) was effective against *Pseudomonas* bacteria and (4) showed good activity against *Salmonella sp.* only. Complex (3) was only complex which showed anti-microbial activity for *E. coli.* and *Pseudomonas*. Results of anti-microbial assessment of complexes are shown in Table 5.

3.6.2. Superoxide dismutase activity

The SOD activity of the present complexes were investigated by NBT assay and catalytic activity towards the dismutation of superoxide anion was measured. IC₅₀ value of the complex (1) is 68 μ mol dm⁻³ (Fig. 7), and the remaining complexes (2), (3) and (4) are 66, 70 and 73 μ mol dm⁻³, respectively these are in the same order of magnitude as the best SOD model complexes [27,28] but higher than the native SOD (0.04 μ mol dm⁻³). The



Fig. 6. Cyclic voltammogram of [Cu(PMDT)(OAc)]BPh₄ in 0.1 M TBAP [scan rate: 100(mV/s)].



Fig. 7. Superoxide dismutase activity of [Cu(PMDT)(OAc)]PF₆.

distorted geometry of complexes may favor the geometrical change, which is essential for the catalysis of copper in the Cu–Zn SOD that also changes distorted square pyramidal geometry [28,29].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 294244 for complex [Cu(PMDT)(OAc)]PF₆ (1). Copies of this information be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB 21 EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc-cam.ac.uk or http://www.ccdc.cam.ac.uk/.

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