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Synthesis and characterization of a copper–zinc heterobinuclear complex of 2,2′-bipyridine

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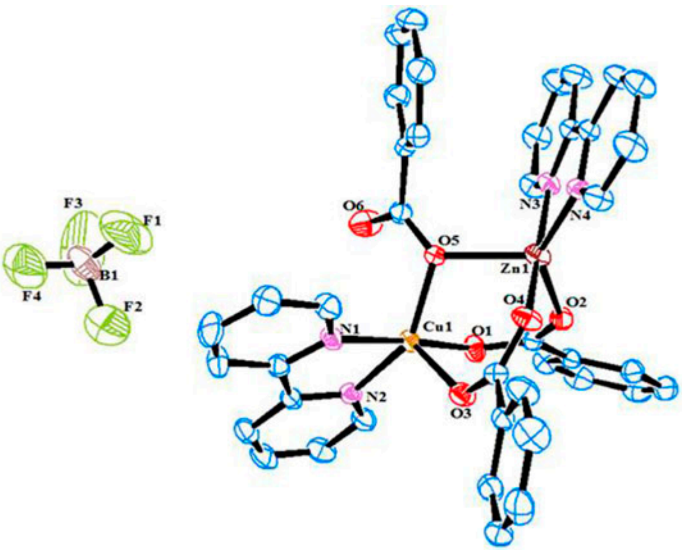

The synthesis of the heterobinuclear copper–zinc complex $[CuZn(bz)_3(bpy)_2]BF_4$ from benzoic acid and bipyridine is described. Single crystal X-ray diffraction of the heterobinuclear complex reveals the geometry of the benzoate-bridged Cu(II)–Zn(II) center. The copper and zinc ions are five coordinates, having distorted square pyramidal geometry. The Cu–Zn distance is 3.384 Å. The complex is normal paramagnetic having μ_{eff} value equal to 1.75 BM, ruling out the possibility of Cu–Cu interaction in the structural unit of the complex. The ESR spectrum of the complex in CH_3CN at RT exhibits an isotropic four-line spectrum centered at $g = 2.082$ and hyperfines coupling constants $A_{av} = 63 \times 10^{-4}\ cm^{-1}$, characteristic of mononuclear square-pyramidal copper(II) complexes. At LNT, the complex shows anisotropic spectra with $g_{\parallel} = 2.260$ and $g = 2.070$ and $A_{\parallel} = 170 \times 10^{-4}\ cm^{-1}$, respectively, characteristic of distorted square-pyramidal geometry. The complex is an efficient catalyst for oxidation of alcohols to aldehydes and ketones.

Keywords: Copper; Zinc; Bipyridine

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Introduction

Copper is an essential trace element which occurs in several important enzymes like cytochrome c-oxidase, ceruloplasmin, carbon monoxide dehydrogenase (CODH), superoxide dismutase, OEC, etc. [1, 2]. In these enzymes, it is present either alone or in combination with other metals like Fe, Zn, Mn, Mo, etc. Copper occurs in ceruloplasmin together with iron [2]. In this enzyme, copper is reduced by Fe^{2+} and then oxidized by molecular oxygen in a cyclic process. In CODH, copper is present with molybdenum. This enzyme catalyzes oxidation of CO to CO_2 [1]. Copper occurs in nature in combination with zinc in superoxide dismutase which is one of the most crucial enzymes in the defense system of organisms for its ability to protect cells from damage of the toxic superoxide ion [3, 4]. The introduction of heterometals into metal clusters may produce more complex clusters with new functions. The heterobimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently or in a different manner to isolated metal centers, monometallic and homobimetallic complexes. Heterobimetallic complexes offer an opportunity to study the cooperative interaction between metal ions.

The perception that heterobinuclear sites of many metalloenzymes including SOD situate their metal centers in chemically distinct environments has motivated us to synthesize heterobinuclear copper(II)–zinc(II) complexes from carboxylate ligands inside the coordination sphere incorporating bidentate ligands. Homobimetallic copper(II) complexes of benzoic acid have been synthesized and characterized, and their crystal structures were established. However, heterobimetallic Cu–Zn complexes containing coordinated benzoic acid and bipyridine inside the coordination sphere have not been synthesized, although a few heterobimetallic Cu–Zn complexes from multidentate ligand systems have been synthesized and characterized [5–7]. Further, as Cu–Zn superoxide dismutase catalyzes the disproportion of toxic ion superoxide in biological systems, it was envisioned that heterometal complexes containing copper and zinc in close proximity might act as a catalyst in oxidation reactions useful in synthetic organic chemistry. Hence, we studied the oxidation of alcohols to aldehydes and ketones mediated by H_2O_2 using complexes isolated in the present study. Herein we describe the synthesis and characterization of a copper–zinc heterobimetallic complex using bpy, including EPR, X-ray structure, UV/visible studies, and catalytic studies. The complex catalyzes the oxidation of alcohols to their corresponding carbonyl compounds. Such catalytic behavior suggests that the complex has potential as an effective oxidation catalyst.

Experimental

All reagents and chemicals were E-Merck, Himedia, or equivalent grades, and all solvents were used as received. All operations were performed under aerobic conditions.

Physical measurements

Copper and zinc were determined by standard literature [8] procedure. C, H, and N were determined by microanalytical method using a Perkin-Elmer 2400 CHNS/O Analyzer 11. Infrared spectra from 4000 to 200 cm^{-1} were recorded as KBr disks by using a BX-III/

FTIR Perkin Elmer spectrophotometer. Infrared spectra in solution state were recorded in chloroform solution. Solid state and solution electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer. Room temperature magnetic data of the powdered sample were measured using a Sherwood Scientific Magnetic Susceptibility Balance. The magnetic data were corrected for diamagnetism using Pascal's constants [9]. Conductance measurements were done using a Wayne Kerr B 95 Automatic Precision Bridge with a dip-type conductivity cell having a platinized platinum electrode. The cell constant was determined using a standard KCl solution. Mass spectra of the complexes were recorded on a Water ZQ-4000 Micromass Spectrometer. X-band EPR spectra at room temperature and at variable temperature were recorded from powdered samples, and from CH_3CN solution on a Varian E-112 ESR Spectrometer using TCNE ($g = 2.0027$) as an internal standard. Gas Chromatographic (GC) analysis was performed on a Bruker 430-GC gas chromatograph equipped with a 30 m × 0.32 mm × 0.5 μm HP-Innowax capillary column and a flame ionization detector.

X-ray crystallography and structure solution

Intensity data for the complex were collected on an X Calibur Oxford Diffractometer with graphite-monochromated Cu Kα radiation. The structures were solved and refined against F^2 with full matrix least-squares using SHELX-97 [10] software using WinGX (Ver 1.80.05) [11] platform. All hydrogens were added at calculated positions and refined by a riding model with isotropic displacement parameters based on those of the parent atom. Anisotropic displacement parameters were employed for all non-hydrogen atoms.

Synthesis

Preparation of $[CuZn(bz)_3(bpy)_2]BF_4$. Bipyridine (0.156 g, 1 mM) solution in methanol (10 cm^3) was slowly added with stirring to $Cu(OAc)_2\cdot H_2O$ (0.1 g, 0.501 mM) in methanol at a temperature of 50–60 °C. After 5 min, a deep blue homogeneous solution was obtained, and to this was added methanolic solution (10 mL) of $Zn(OAc)_2\cdot(H_2O)_2$ (0.11 g, 0.5 mM), followed by addition of $NaBF_4$ (0.110 g, 1 mM) solution in methanol with continuous stirring. To the blue solution so obtained, benzoic acid (0.112 g, 1 mM) solution in methanol (10 mL) was added and the reaction mixture was stirred for another 5 min. The reaction mixture was filtered and kept undisturbed. Deep blue crystals started depositing after 2–3 h. The product was recrystallized from CH_3CN. The yield of the product was 70.9%. The above reaction was again carried out maintaining the molar ratio of $Cu(OAc)_2\cdot H_2O : Zn(OAc)_2\cdot 2H_2O$: bpy : benzoic acid and $NaBF_4$ at 1 : 1 : 3 : 2 : 2. The same reaction product was obtained. The yield improved to 91.2%. Yield: 91.2%. Anal *(%)*, Calcd *for* $C_{41}H_{31}N_4O_{10}CuZnBF_4$: C, 55.19; H, 3.48; N, 6.28; Cu, 7.35; Zn, 7.34. Found: C, 54.40; H, 3.50; N, 6.46; Cu, 7.35; Zn, 7.60. IR data (cm^{-1}, KBr): 1619 (s), 1569(vs), 1447 (s), 1387 (m), 1082 (vs), 729 (vs), 679 (s), 1082 sbr (ν BF_4^-). Mass (*m/z*): expt. 804.92, theo. 804.65. *Molar conductance* (Ω^{-1} M^{-1} cm^2): 130. *Magnetic Moment* (μB): 1.77 *Solid-state (diffuse reflectance) electronic spectrum* (λ_{max}, nm): 860. *Electronic spectrum* [λ_{max}, nm (ε_{max}, dm^3 M^{-1} cm^{-1})]: in MeCN, 693 (150).

Experimental procedure for the oxidation of benzyl alcohol

A general procedure for the oxidation of benzylic alcohols follows

To a mixture of benzyl alcohol (0.5 mL, 4.84 mM) and 30% aqueous hydrogen peroxide (0.5 mL, 4.63 mM), the complex $[CuZn(bz)_3(bpy)_2]BF_4$ (20 mg, 0.22 mM) was added and stirred at 70 °C for 6 h and the reaction mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate. Evaporation of dichloromethane gave a crude mixture for ^1H NMR analysis, then was purified by column chromatography to afford benzaldehyde, whose identity was ascertained by comparison with authentic sample and IR, ^1H NMR, and ^{13}C NMR.

Characterization data for benzaldehyde

Colorless liquid; yield: 424 mg, 86.4 %; ^1H (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.87–7.41 (m, 5H); ^{13}C (100 MHz, $CDCl_3$): δ192.5, 136.2, 134.4, 129.8, 128.9; Ir (KBr): 1702 cm^{-1}.

Results and discussion

The complex was obtained when $Cu(OAc)_2{\cdot}H_2O : Zn(OAc)_2{\cdot}2H_2O$: bpy : benzoic acid and $NaBF_4$ were allowed to react in 1 : 1 : 2 : 2 : 2 M ratio in methanol at 50–60 °C. The complex was recrystallized from CH_3CN. This reaction was reproducible and in all preparations, deep blue complex crystallized from the reaction mixture. The complex was identified by elemental analysis and mass spectroscopy. The observed *m/z* value 804.92 (theo. 804.65) in the mass spectrum clearly demonstrates the formation of the heterobinuclear complex $[CuZn(\mu_2\text{-}C_6H_5COO)_2(\mu_1\text{-}C_6H_5COO)(bpy)_2]BF_4$ rather than a mixture of homonuclear copper and zinc complexes. The complex is insoluble in benzene, hexane, toluene, CCl_4, and ether. The complex is sparingly soluble in water and completely soluble in methanol, acetonitrile, and DCM.

Molar conductance

The molar conductivity of the complex was 130 Ohm^{-1} M^{-1} cm^2 at 10^{-3} M dilution in acetonitrile. This value suggested that the complex is 1 : 1 electrolyte in this medium [12].

Description of structure

The ORTEP view of the heterodinuclear complex is shown in figure 1. Crystal and structure refinement data are presented in table 1. Selected bond distances and angles of the complex are summarized in table 2. The complex consists of a dinuclear $[(C_6H_5COO)_3(bpy)_2CuZn]^+$ cation and a well-separated tetrafluoroborate anion. In the cation, Cu and Zn are bridged by two benzoate groups in the bidentate η^1, η^1, μ_2-bridging and the third is monodentate bridging. Copper(II) and zinc(II) have five-coordinate structures.

The Cu(II) site comprises the O(1), O(5), N(1), N(2), and O(3) atoms, while zinc(II) comprises O(2), O(4), O(5), N(3), and N(4). The *trans* angles around Cu(1) are O(1)–Cu

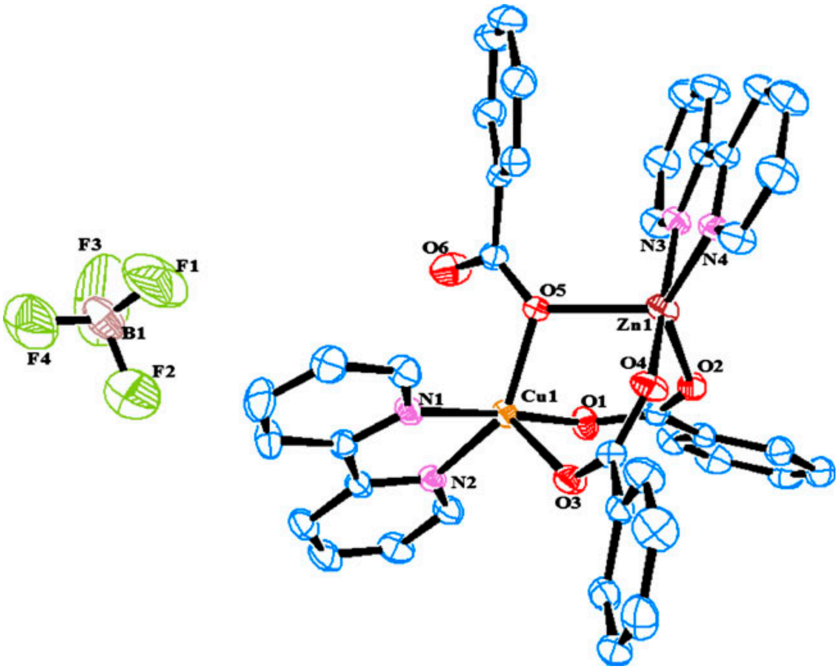


Figure 1. Thermal ellipsoid plot of the complex at 30% probability level (H atoms are removed for clarity).

Table 1. Crystal data and refinement parameters.

Parameters	Complex
Formula	$C_{41}H_{31}BCuF_4N_4O_6Zn$
FW	891.42
Temperature	293(2)
Wavelength	1.541
Crystal system	Monoclinic
Space group	*P2₁/c*
a (Å)	11.5252(4)
b (Å)	21.4874(7)
c (Å)	15.9192(5)
β	109.215(4)
Volume	3722.7(2)
Z	4
Density (calculated)	1.590
Abs. coeff.	2.151 mm^{-1}
F(0 0 0)	1812
Crystal size	0.34 × 0.33 × 0.32 mm^3
Θ range for data collection	4.55–72.41
Index ranges	$-13 \leq h \leq 14$
	$-15 \leq k \leq 26$
	$-19 \leq l \leq 14$
Reflections collected	6952
Refinement on F^2	Full matrix least-squares
Goodness of fit on F^2	1.017
Final *R* indices	$R_1 = 0.0732$, $WR_2 = 0.1674$
	$R_2 = 0.0533$, $WR_2 = 0.1484$

Table 2. Selected bond distances (Å) and angles (°) for complex.

Bond distances (Å)					
Cu–Zn 3.384					
Cu(1)–N(1)	2.001(3)	C(15)–O(5)	1.294(4)	Zn(1)–O(2)	1.995(2)
Cu(1)–N(2)	2.030(3)	C(15)–O(6)	1.217(5)	Zn(1)–O(4)	1.928(3)
Cu(1)–O(1)	1.954(3)	C(8)–O(3)	1.243(5)	Zn(1)–O(5)	2.167(2)
Cu(1)–O(3)	2.166(3)	Zn(1)–O(6)	4.173	C(1)–O(1)	1.267(4)
Cu(1)–O(5)	1.980(3)	Zn(1)– N(3)	2.011(3)	C(1)–O(2)	1.247(4)
Cu(1)–O(6)	2.844	Zn(1)–N(4)	1.997(3)	C(8)–O(4)	1.243(5)
Bond angles (°)					
Zn(1)–O(5)–Cu(1) 109.31(11)					
O(1)–Cu(1)–O(5)	96.7(1)	C(31)–N(2)–Cu(1)	126.7(3)	O(2)–Zn(1)–O(5)	89.78(1)
O(1)–Cu(1)–N(1)	171.9(1)	C(27)–N(2)–Cu(1)	114.2(3)	N(4)–Zn(1)–O(5)	121.76(1)
O(5)–Cu(1)–N(1)	89.5(1)	C(22)–N(1)–Cu(1)	124.2(3)	N(3)–Zn(1)–O(5)	89.12(1)
O(1)–Cu(1)–N(2)	91.7(1)	C(26)–N(1)–Cu(1)	115.4(3)	C(15)–O(5)–Zn(1)	130.3(2)
O(5)–Cu(1)–N(2)	148.5(1)	O(2)–C(11)–O(1)	125.9(3)	C(31)–N(2)–Zn(1)	124.8(3)
N(1)–Cu(1)–N(2)	80.3(1)	O(4)–C(8)–O(3)	126.6(4)	C(8)–O(4)–Zn(1)	129.7(3)
O(1)–Cu(1)–O(3)	95.5(1)	O(4)–Zn(1)–O(2)	95.0(1)	C(1)–O(2)–Zn(1)	133.5(2)
O(5)–Cu(1)–O(3)	95.9(1)	O(4)–Zn(1)–N(4)	91.8(1)	C(37)–N(4)–Zn(1)	115.2(3)
N(1)–Cu(1)–O(3)	89.1(1)	O(2)–Zn(1)–N(4)	141.3(1)	C(41)–N(4)–Zn(1)	126.3(3)
N(2)–Cu(1)–O(3)	113.5(1)	O(4)–Zn(1)–N(3)	172.1(1)	C(32)–N(3)–Zn(1)	126.4(3)
C(15)–O(5)–Cu(1)	112.1	O(2)–Zn(1)–N(3)	92.5(1)	C(36)–N(3)–Zn(1)	114.1(3)
C(1)–O(1)–Cu(1)	127.2(3)	N(4)–Zn(1)–N(3)	80.8(1)	O(6)–C(15)–O(5)	122.9(4)
C(8)–O(3)–Cu(1)	129.0(3)	O(4)–Zn(1)–O(5)	92.4(1)	O(4)–C(8)–O(3)	127.3(4)

(1)–N(1), 171.9(1) and O(5)–Cu(1)–N(2), 148.5(1)°, while around Zn(1), the *trans* angles are O(2)–Zn(1)–N(4), 141.3 (1) and O(4)–Zn(1)–N(3), 172.1(1). The first *trans* angle around copper is closer to linear than the second one, which considerably deviates from linearity. Similarly, the *trans* angles around the Zn(1) site O(4)–Zn(1)–N(3), 172.1 (1)° and O (2)–Zn(1)–N(4), 141.3(1) are close to linear and considerably deviated from linear, respectively. These values of angles suggested distorted square pyramidal structure around Cu and Zn ions. The basal plane around Cu ion is composed of the bridging benzoates O(1) and O (5) and the bipyridine nitrogens N(1) and N(2). The basal plane around Zn is composed of O(2), O(4), N(4), N(3) oxygens from bridging benzoate and nitrogen originating from bipyridine. The apical position on Cu is occupied by bidentate-bridged benzoate O(3) while that on Zn is occupied by monodentate-bridged benzoate O(5). The distance of the metal centers from the monodentate bridging benzoate oxygen Cu(1)–O(5), 1.980(3) Å and Zn (1)–O(5) 2.167(2) Å are quite different as are the distances from bipyridyl nitrogens Cu(1)–N(1), 2.001(3) Å, Cu(1)–N(2), 2.030(3), Zn(1)–N(3), 2.011(3) Å, and Zn(1)–N(4), 1.997 (3) Å.

The parameter Γ represents the degree of trigonality within the structural continuum between square pyramid ($\Gamma = 0$) and trigonal bipyramidal structure ($\Gamma = 1$) [12]. The Γ value is obtained as $\Gamma_1 = 0.39$ in the Cu(II) site and as $\Gamma_2 = 0.52$ in the Zn(II) site by using the equation $\Gamma = (\beta - \alpha)/60$, where α_1 = O(5)–Cu(1)–N(2) 148.5(1), β_1 = O(1)–Cu(1)–N(1), 171.9(1) and α_2 = O(2)–Zn(1)–N(4), 141.3(1), β_2 = O(4)–Zn(1)–N(3), 172.1(1), respectively. Thus, the coordination geometry of Cu(II) in the complex can be described as distorted square pyramidal [13] whereas that of Zn(II) is trigonally distorted square-based pyramidal geometry [13], i.e. both the metal centers have distorted square pyramidal geometry with more distortion in the zinc(II) center (figure 2).

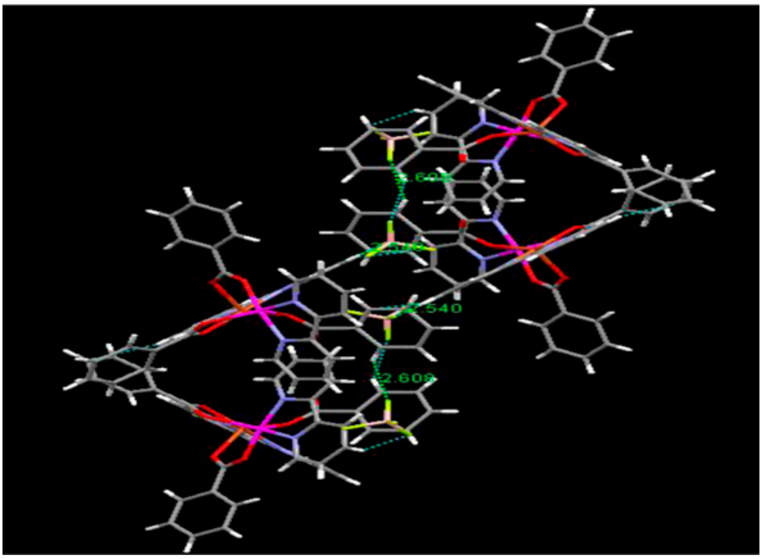


Figure 2. Packing diagram of the complex viewed along the *c*-axis.

The bridging mode for one benzoate results in a significant difference between the length of the two carboxylate CO bonds [14], the C(15)–O(5) distance (1.294(4) Å) being larger than the C(15)–O(6) distance (1.217(5) Å). In monoatomic bridging $RCOO^-$ groups, there is evidence for an additional weak interaction [15]. In the heterobimetallic complex, this weak interaction is manifested in the Cu(1)–O(6) distance between the Cu(1) and the non-bridging carboxylato oxygen O(6). The Cu(1)–O(6) distance is 2.844 Å, as against that of Zn(1)–O(6) distance 4.173 Å. This shows that only one benzoate is clearly shifted toward Cu(1). This is manifested in the Cu(1)–O(5)–C(15) angle (112.1(2)) being significantly smaller than Zn(1)–O(5)–C(15) (130.3(2)) Å. Also the Cu(1)–O(5) bridging distance (1.980 (2) Å) is noticeably shorter than the Zn(1)–O(5) bridging distance (2.167(2) Å). This might be inherent in the Jahn–Teller effect. Due to distorted square pyramidal structure around copper, the unpaired electron might spend substantial time in the $d_z{}^2$-orbital having axial orientation in the ground state. This allows the O(5) donor in the axial direction to move towards copper giving smaller Cu–O(5) distance than those in the equatorial direction. Further, the coordination geometries of Cu^{II} and Zn^{II} ions are slightly different with the geometry around Cu(1) having more square pyramidal character than that around Zn(1). We attribute this difference due to the Cu(1)–O(6) interaction. The geometry of Cu(1) is best described as compressed distorted square-based pyramid with O(5) at the apex as expected, the axial bond is about (1.976 Å), shorter than bond lengths in the basal plane. The Cu–N and Zn–N distances and their slight variation as a function of axial *versus* equatorial location of Cu(1) and Zn(1) are typical of Cu^{II}–bpy [16] and Zn^{II}–bpy complexes [17].

Monoatomic bridging for benzoate is not known in heterometal chemistry, albeit the monoatomic-bridging mode for acetate in copper(II) acetate chemistry and other carboxylate ligands is documented in the literature. In the complex, Cu–Zn separation is 3.384 Å, but the largest Cu–O–Zn bond angle (109.3(1)) for the complex is less as compared to Cu–Cu separation (3.392 Å) in the corresponding homobimetallic complex containing acetate groups in the coordination sphere [18].

In the complex, the average Zn–N bond length (1.997(3), 2.011(3) Å) is slightly shorter than that of Cu–N bond (2.001, 2.030 Å). The axial Zn–O(5) bond length along with equatorial orientation of the square pyramid (Cu–O(5) 1.980(3)) Å is noticeably shorter than the Zn–O(5) distance (2.167(2) Å). This is in complete agreement with literature values 1.977 (2) and 2.169(2) in Christou's acetate complex $[Cu_2(CH_3COO)_3(bpy)_2]ClO_4$ [18]. The distance of Zn–O(5) (2.167(2) Å) is consistent with the longer length normally observed in the axial direction of the TP. In view of the little difference between average Cu–L and Zn–L bond lengths and the same coordination geometries around the metals with similar distortions, the possibility of interchanging the Cu and Zn ions in the same molecule cannot be eliminated [19].

Magnetic moment

At room temperature, the Cu(II) complex has magnetic moment value equal to 1.77 μB. This magnetic moment value is very close to the spin-only value of 1.73 μB, ruling out the possibility of any appreciable spin–spin interaction between copper centers. Further, this value suggests that the complex is monomeric in nature.

ESR

The spectrum of the complex in CH_3CN at LNT is shown in figure 3. The polycrystalline sample shows a simple isotropic signal at $g = 2.082$ at RT. However, the spectrum in CH_3CN solution at RT is a four-line spectrum characteristic of mononuclear copper(II) complexes with $I = 3/2$. The g_{av} value is 2.150. The copper hyperfine constant A_{Cu} is 64 G.

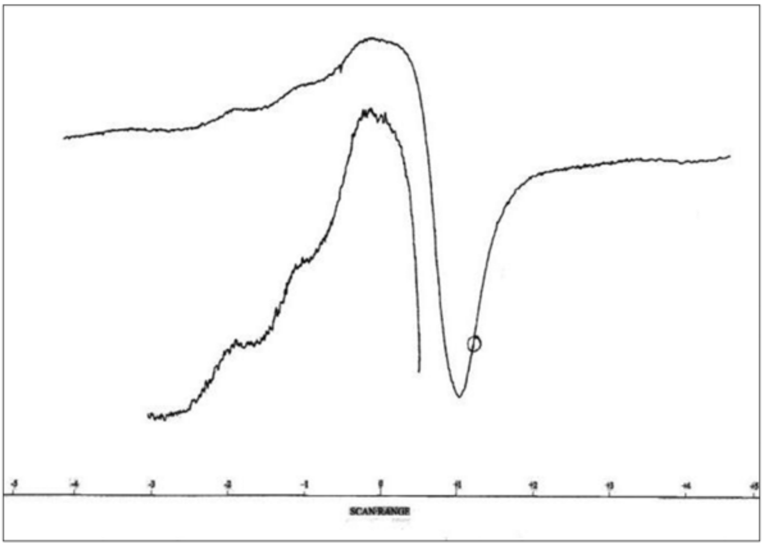


Figure 3. ESR spectrum of the complex in CH_3CN solution at LNT ($f = 9.1$ GHz).

The hyperfine coupling constant <A> = 64 G is typical of a mononuclear copper(II) complex. This is even reflected in the frozen solution (77 K) spectrum with two hyperfine lines in $g_\parallel$ region in complex, characteristic of an axially symmetric anisotropy. The observed Hamiltonian parameters are $g_\parallel = 2.260$, $g_\perp = 2.070$, $g_{av} = 2.132$, $A_\parallel = 170$G, and $g_\parallel/A_\parallel = 142$ cm for complex. The observed trend indicates a d_{x2-y2} ground state with tetragonal site symmetry for Cu(II) in the complex as expected from the structural and ligand features [20]. The Hamiltonian parameters for the complex are similar to those of the reported imidazolate-bridged Cu–Zn heterobimetallic complex [8, 20]. The spectra of the complexes are very similar to that of (Cu_2Zn_2SOD) having a $g_\parallel/A_\parallel$ value of 142 cm for which arrangement around copper ion intermediate between a trigonal bipyramid and a square pyramid has been postulated [20]. The ratio $g_\parallel/A_\parallel$ for the complexes is 142. These values are very close to the range 90–140 cm for square planar equatorial configuration suggesting that in the complex, there is only slight distortion in the equatorial plane.

IR Spectra

The complex shows strong bands at 1612 and 1569 cm^{-1} with other strong bands at 1447 and 1387 cm^{-1}. These bands are assigned to ν_{as}(COO) and ν_s(COO) stretching modes, respectively. The difference between 1568 and 1447 cm^{-1} is 122 cm^{-1} which is less than that for NaO_2Me (164 cm^{-1}) [21, 22]. Hence, these bands are attributed to triatomic acetate bridges. A large splitting ($\Delta = 229$ cm^{-1}) between the stretching frequencies (1612 cm^{-1}) and (1383 cm^{-1}) is observed. Hence, they are attributed to ν_{as}(COO) and ν_s(COO) stretching modes of the monoatomic acetate bridge [21(a)]. The complex shows a single strong band at 729 cm^{-1} attributed to out-of plane motion of the hydrogens as expected for two identical groups of four hydrogens each [21(b)]. Apart from this band, the complex shows a medium intensity band at 679 cm^{-1} [23], assigned to in-plane ring deformation mode of 2,2′-bipyridine. These pieces of evidences indicate coordination of 2,2′-bipyridine to the metal center [21, 22]. The BF_4^- at ~1100 cm^{-1} in free anion appears at 1082 cm^{-1} as a strong band, indicating its non-coordinated nature in the complex.

Electronic spectra

The complex exhibits benzoate-to-copper LMCT transition at 340 nm [24]. The electronic spectrum of the complex in polycrystalline state exhibits a broad band at 650–950 nm with center at 860 and 830 nm (with weaker shoulder at 890 nm). This band is assigned to d–d transition [24]. These data suggest a tetragonal pyramidal coordination geometry for copper. This broad band appears to be the envelope of bands arising from $B_1 \rightarrow E$, $B_1 \rightarrow B_2$, and $B_1 \rightarrow A_1$ transitions, respectively [24]. The energies of the d–d transitions in tetragonal pyramid chromophores usually lie from 590 to 770 nm as compared to bands at 710 and 765 nm in the corresponding binuclear copper(II) complex. In this complex, red shift of electronic transition may be attributed to the influence of bidentate bipyridine in the complex [25]. Christou's complex [18] showed the presence of two bands at 710 and 765 nm indicating the presence of two copper ions in different stereochemistry. The presence of a single d–d band in our complexes further confirms the presence of only one copper center in the complex.

In CH_3CN solution, a d–d band at 693 (150 M^{-1} dm^3 cm^{-1}) which is asymmetrical is observed [24]. The essential feature of this band together with molar extinction coefficient suggests that the complex has less tetragonally distorted square pyramidal stereochemistry in CH_3CN solution.

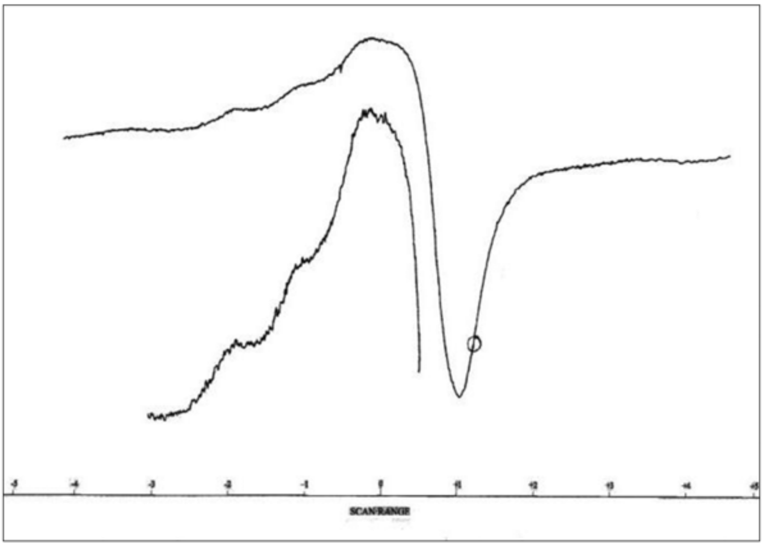
Reactivity study

The selective oxidation of alcohols to their corresponding carbonyl compounds is a fundamental transformation in organic synthesis [26]. In particular, the conversion of primary alcohols to aldehydes is crucial in the synthesis of natural products and fine chemicals such as fragrances and food additives [27]. Keeping in view the fact that copper and zinc are the catalytic center in several metalloenzymes [1, 2, 28], and both are present together in superoxide dismutase [1] and the fact that the metal complexes serve as catalyst in oxidation of alcohols to aldehydes and ketones [29–31], it was worthwhile to investigate the catalytic activity of the present heterobimetallic complex. Accordingly, the catalytic activity of the complex towards the hydrogen peroxide mediated oxidation of primary alcohol viz, benzyl alcohol was studied and the results reported.

The initial study was carried out using benzyl alcohol as substrate (4.63 mM) and 1.91 equivalent of H_2O_2 (8.83 mM) at ambient temperature in the presence of 0.022 mM of catalyst (scheme 1).

The oxidation reaction was conducted at 70 °C keeping $[CuZn(bz)_3(bpy)_2]BF_4$: benzyl alcohol : H_2O_2 molar ratio at 1 : 209.5 : 398.2. The results reveal that this heterobinuclear complex efficiently catalyzes the oxidation of benzyl alcohol to the aldehyde in good yield (86.4%). Fortunately, the usual undesirable further oxidation to acid was not observed under the present reaction conditions.

The experimental results indicated that complex is an efficient catalyst for abstraction of two hydrogens from the substrate. The catalyst did not induce the unproductive decomposition of H_2O_2 to any great extent and enables the economic use of the oxidant. After a



Scheme 1.

mixture of benzyl alcohol (0.5 g, 4.63 mM) and 30 % H_2O_2 (1 mL, 8.83 mM) was vigorously stirred in air at room temperature for 6 h, there was no consumption of H_2O_2 and neither benzaldehyde nor benzoic acid was obtained; only benzyl alcohol was recovered after work up of reaction mixture.

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