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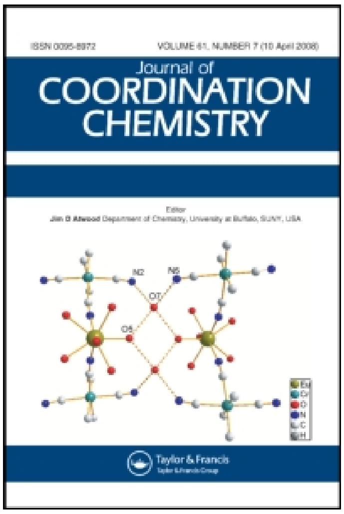

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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Synthesis, structure and SOD-like activity of a ternary Cu(II) complex with 1,10-phenanthroline and *L*-valinate

Xueyi Le[a]; Shenrong Liao[a]; Xiaopin Liu[a]; Xiaolong Feng[b]
[a] Department of Applied Chemistry, College of Sciences, South-China Agricultural University, Guangzhou, Guangdong 510642, P.R. China [b] Center of Analysis and Measurement, Zhongshan University, Guangzhou, Guangdong 510275, P.R. China

To cite this Article Le, Xueyi , Liao, Shenrong , Liu, Xiaopin and Feng, Xiaolong(2006) 'Synthesis, structure and SOD-like activity of a ternary Cu(II) complex with 1,10-phenanthroline and *L*-valinate', Journal of Coordination Chemistry, 59: 9, 985 — 995

To link to this Article: DOI: 10.1080/00958970500443144

URL: http://dx.doi.org/10.1080/00958970500443144

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Journal of Coordination Chemistry
Vol. 59, No. 9, 15 June 2006, 985–995

Synthesis, structure and SOD-like activity of a ternary Cu(II) complex with 1,10-phenanthroline and *L*-valinate

XUEYI LE*†, SHENRONG LIAO†,
XIAOPIN LIU† and XIAOLONG FENG‡

†Department of Applied Chemistry, College of Sciences,
South-China Agricultural University, Guangzhou,
Guangdong 510642, P.R. China
‡Center of Analysis and Measurement, Zhongshan University, Guangzhou,
Guangdong 510275, P.R. China

(*Received 4 April 2005; in final form 5 July 2005*)

The ternary Cu(II) complex with 1,10-phenanthroline (phen) and *L*-valinate (*L*-Val) has been synthesized and investigated by elemental analysis, molar conductivity, UV/vis, IR, TG-DTG, and X-ray diffraction methods. The complex crystallizes in the triclinic space group $P1$ with two molecules in a unit cell of dimensions, $a = 7.157(2)$ Å, $b = 11.967(4)$ Å, $c = 12.249(4)$ Å, $\alpha = 68.290(4)^\circ$, $\beta = 77.813(5)^\circ$, $\gamma = 83.490(5)^\circ$, $V = 0.952.0(5)$ nm Å^3, $R_1 = 0.0297$, and $wR_2 = 0.0396$. The crystal contains two crystallographically independent $[Cu(H_2O)(L\text{-Val})(phen)]^+$ subunits **Cu1** and **Cu2**, having a distorted square-pyramidal geometry with the same coordinated atoms around each copper center, the base plane being occupied by two nitrogen atoms of one phen, the amino nitrogen atom and one carboxylate oxygen atom from each independent *L*-Val moiety, and one water oxygen at an axial position. The SOD-like activity of the complex has been measured by means of modified nitroblue tetrazolium (NBT) photoreduction, and the IC_{50} value (the concentration of the complex which causes the 50% inhibition of NBT reduction) of the complex for disproportionation of $\overline{O}_2^{\bullet}$ is 2.48×10^{-7} M. The experimental results show that the complex is a potent superoxide dismutase mimic. CCDC: 267641.

Keywords: 1,10-Phenanthrolin; *L*-valinate; Copper(II) complex; Crystal structure; SOD-like activity

1. Introduction

Superoxide anion $\overline{O}_2^{\bullet}$ is essential for the biological defense system against the invasion of bacteria and viruses. On the other hand, the superoxide anion has been known to be important in the pathogenesis of many disease processes, including inflammatory damage [1], membrane and DNA damage [2], and aging [3]. A critical balance

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*Corresponding author. Email: lexy@scau.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500443144

of enzymes defending against antioxidants such as SODs is therefore required to maintain normal cell and organ function. Although there is much interest in the use of SOD for pharmaceutical purposes, its practical use in biological systems is problematic due to difficulties associated with the systematic infection of protein, i.e. the circulation lifetime, cell impermeability, immunogenicity, tissue targeting, antigenicity, and high costs. To circumvent such limitations, there has been considerable interest in developing synthetic SOD mimics that have low molecular weight, biological stability, membrane permeability, and are nontoxic and cost-effect [4, 5].

Based on copper complexes with aminoacids and phenanthroline having been proposed as SOD-like compounds [6, 7], in this work, the complex $[Cu(H_2O)(L\text{-Val})(phen)]Cl \cdot H_2O$ (*L*-Val = *L*-valinate group, phen = 1,10-phenanthroline) has been synthesized and investigated by elemental analysis, molar conductivity, UV/vis, IR, TG-DAG, and single crystal X-ray diffraction methods. The SOD-like activity of the complex has been measured by means of modified nitroblue tetrazolium (NBT) photoreduction, the experimental results show that the phen–copper-amino acid complex has a distinct SOD-like activity in water.

2. Experimental

2.1. *Materials*

All chemicals were of reagent grade quality and used without further purification.

2.2. *Synthesis*

The complex was prepared by reaction of $CuCl_2 \cdot 26H_2O$ (0.1705 g, 1 mmol) and 1,10-phenanthroline monohydrate (0.1982 g, 1 mmol) in 10 mL of aqueous ethanol, followed by addition of 5 mL of aquous solution of *L*-valine (0.1172 g, 1 mmol) and NaOH (0.0400 g, 1 mmol). The solution was stirred for 30 min at room temperature and filtered. The resulting solution was left to evaporate at room temperature. Blue crystals formed after a month. The crystals were filtered and air-dried. Yield: 73%. Anal. for $C_{17}H_{22}ClCuN_3O_4$ (%). Calcd C, 47.33; H, 5.14; N, 9.74. Found: C, 47.12; H, 5.19; N, 9.80.

2.3. *Physical measurements*

Microanalysis (carbon, nitrogen and hydrogen) was carried out on a Perkin-Elmer 240C microanalyzer, and molar conductivity measurement was performed in ethanol with a DDS-11A conductivity gauge. The infrared absorption spectrum in KBr disks was measured in the $4000 \sim 400\,cm^{-1}$ range with a Nicolet 170SX spectrophotometer. The electronic absorption spectrum of the complex was recorded in ethanol on a Pharmacia 4000 UV-Vis spectrophotometer at room temperature. TG-DTA was performed on a METZSCH TG 209 apparatus. The sample was contained within alumina crucibles and heated at a rate of $10^{\circ}C\,min^{-1}$ from room temperature to 470°C under air condition.

Table 1. Crystallographic data of the complex $[Cu(H_2O)(L\text{-val})(phen)]Cl \cdot H_2O$.

Formula	$C_{17}H_{22}ClCuN_3O_4$
Formula weight	431.37
Temperature (K)	293 (2)
Crystal size (mm^3)	$0.34 \times 0.29 \times 0.23$
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions (Å, °)	$a = 7.157(2)$; $\alpha = 68.290(4)$ $b = 11.967(4)$; $\beta = 77.813(5)$ $c = 12.249(4)$; $\gamma = 83.490(5)$
Volume ($Å^3$), Z	952.0(5), 2
D_c ($g\,cm^{-3}$)	1.505
μ (mm^{-1})	1.358
$F(000)$	1011
θ range for data collection	1.82 to 27.05°
Range of h, k, l	$-9 \le h \le 9$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections collected/Unique	8101/7230 ($R_{int} = 0.0192$)
Completeness to $\theta = 27.05°$	98.1%
Absorption correction	Semi-emipirical
Max. and min transmission	0.7520, 0.6635
Refinement method	Full-matrix least-squares on F^2
Refined parameters	475
Goodness-of-fit on F^2	1.002
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0297$, $wR_2 = 0.0661$
R indices (all data)	$R_1 = 0.0396$, $wR_2 = 0.0701$
Absolute structure parameter	0.030(10)
Mar., min. height in final ΔF map ($e\,Å^{-3}$)	0.250, −0.458

2.4. *X-ray structural determination*

Details of the structure solution and refinement for the complex are shown in table 1.

A single crystal ($0.34 \times 0.29 \times 0.23\,mm^3$) of the complex was selected for X-ray diffraction measurement on a Bruker Smart 1K CCD diffractometer with graphite monochromated Mo-Kα radiation at $\lambda = 0.71073$ Å. The SMART program was applied to search for diffraction peaks to determine cell parameters, and the collected data were reduced using the SAINT+ program [8]. Absorption corrections were applied with the Siemens Area Detector ABSorption (SADABS) program [9].

The structure was solved by direct and Fourier methods, and refinements were carried by full-matrix least squares on F^2 with positional and anisotropic thermal parameters. The atomic coordinates and anisotropic thermal parameters for nonhydrogen atoms were refined to converge. All hydrogen atoms were placed in calculated positions. Atomic scattering factors were taken from International Tables for X-ray Crystallography [10]. All calculations were performed on a PC with the Siemens SHELXS97 [11] and SHELXL97 [12] program packages. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in table 2. The selected bond lengths and angles are collected in table 3.

2.5. *Measurement of SOD activity*

SOD-like activity of the complex was determined by the modified nitroblue tetrazolium (NBT) photoreduction [13]. Solutions containing the complex ($10^{-6} \sim 10^{-8}$ M),

Table 2. Fractional atomic coordinates ($\times 10^4$ Å) and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for the complex.

Atom	x	y	z	U_{eq}
Cu(1)	3611(1)	8646(1)	4852(1)	30(1)
Cu(2)	8765(1)	907(1)	9797(1)	31(1)
Cl(1)	3675(2)	3467(1)	8285(1)	45(1)
Cl(2)	9013(2)	6116(1)	6178(1)	54(1)
C(1)	4179(7)	11224(5)	4481(5)	45(1)
C(2)	4402(7)	12160(5)	4870(5)	54(2)
C(3)	4268(7)	11920(5)	6072(5)	46(1)
C(4)	3891(7)	10771(5)	6872(5)	39(1)
C(5)	3700(7)	10407(5)	8155(5)	47(1)
C(6)	3354(7)	9275(5)	8869(4)	45(1)
C(7)	3185(6)	8359(5)	8416(4)	35(1)
C(8)	2876(7)	7132(5)	9114(4)	49(1)
C(9)	2736(8)	6325(5)	8600(4)	47(1)
C(10)	2865(7)	6744(4)	7359(4)	36(1)
C(11)	3321(6)	8674(4)	7198(4)	31(1)
C(12)	3674(6)	9882(5)	6407(4)	32(1)
C(13)	3670(6)	8966(5)	2540(4)	32(1)
C(14)	3874(5)	7608(3)	3137(3)	33(1)
C(15)	3084(8)	6878(5)	2547(5)	46(1)
C(16)	945(6)	7059(4)	2610(4)	61(1)
C(17)	3666(7)	5565(4)	3024(4)	68(1)
C(18)	9423(7)	2768(5)	7285(5)	46(1)
C(19)	9582(8)	3131(5)	6048(5)	52(2)
C(20)	9407(7)	2322(5)	5544(4)	52(2)
C(21)	9067(7)	1121(5)	6267(4)	44(1)
C(22)	8858(8)	195(6)	5835(5)	54(2)
C(23)	8515(7)	−938(6)	6600(6)	54(2)
C(24)	8318(7)	−1257(5)	7855(5)	46(1)
C(25)	7913(7)	−2419(5)	8728(6)	56(2)
C(26)	7705(7)	−2588(5)	9887(6)	56(2)
C(27)	7929(7)	−1658(5)	10263(5)	43(1)
C(28)	8523(6)	−363(4)	8299(5)	33(1)
C(29)	8910(6)	834(5)	7509(4)	33(1)
C(30)	9069(7)	571(5)	12094(4)	38(1)
C(31)	10164(5)	1725(3)	11369(3)	38(1)
C(32)	9797(10)	2643(5)	12005(5)	70(2)
C(33)	7829(10)	3233(5)	12004(5)	115(2)
C(34)	11325(11)	3593(5)	11440(5)	133(3)
N(1)	3813(5)	10117(4)	5236(3)	36(1)
N(2)	3194(5)	7880(4)	6650(3)	30(1)
N(3)	3159(5)	7264(3)	4431(3)	30(1)
N(4)	9123(5)	1652(4)	7992(3)	34(1)
N(5)	8334(5)	−562(4)	9484(3)	32(1)
N(6)	9779(5)	2217(3)	10122(3)	32(1)
O(1)	3477(5)	9590(3)	3196(3)	40(1)
O(2)	3810(5)	9421(3)	1435(3)	45(1)
O(3)	8644(5)	18(3)	11464(3)	39(1)
O(4)	8762(5)	221(3)	13175(3)	52(1)
O(5W)	6744(4)	8236(3)	4466(3)	48(1)
O(6W)	5717(4)	1518(3)	10217(3)	50(1)
O(7W)	5481(5)	5111(3)	5597(3)	55(1)
O(8W)	7281(6)	4522(4)	8913(4)	69(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths and hydrogen bonding (Å) and angles (°) for the complex.

Cu(1)–O(1)	1.940(3)	Cu(2)–O(3)	1.909(3)
Cu(1)–N(1)	2.011(4)	Cu(2)–N(4)	2.025(4)
Cu(1)–N(2)	2.017(4)	Cu(2)–N(5)	2.000(4)
Cu(1)–N(3)	1.982(3)	Cu(2)–N(6)	1.996(3)
Cu(1)–O(5W)	2.229(3)	Cu(2)–O(6W)	2.237(3)
C(13)–O(2)	1.245(6)	C(30)–O(4)	1.211(6)
C(13)–O(1)	1.264(6)	C(30)–O(3)	1.283(6)
C(13)–C(14)	1.519(6)	C(30)–C(31)	1.534(6)
C(14)–N(3)	1.471(4)	C(31)–N(6)	1.493(4)
O(6W) ··· O(2a)	2.745(5)	O(5W) ··· O(4b)	2.696(4b)
O(1)–Cu(1)–N(3)	84.6(2)	O(3)–Cu(2)–N(6)	85.2(2)
O(1)–Cu(1)–N(1)	92.5(2)	O(3)–Cu(2)–N(5)	92.0(2)
N(3)–Cu(1)–N(1)	174.2(2)	N(6)–Cu(2)–N(5)	167.3(2)
O(1)–Cu(1)–N(2)	166.8(2)	O(3)–Cu(2)–N(4)	171.9(2)
N(3)–Cu(1)–N(2)	100.4(2)	N(6)–Cu(2)–N(4)	99.1(2)
N(1)–Cu(1)–N(2)	81.2(2)	N(5)–Cu(2)–N(4)	82.1(2)
O(1)–Cu(1)–O(5W)	93.9(2)	O(3)–Cu(2)–O(6W)	88.4(2)
N(3)–Cu(1)–O(5W)	88.7(2)	N(6)–Cu(2)–O(6W)	93.3(1)
N(1)–Cu(1)–O(5W)	96.5(2)	N(5)–Cu(2)–O(6W)	98.9(2)
N(2)–Cu(1)–O(5W)	98.2(2)	N(4)–Cu(2)–O(6W)	97.9(2)
C(1)–N(1)–Cu(1)	128.0(3)	C(18)–N(4)–Cu(2)	129.8(3)
C(12)–N(1)–Cu(1)	113.2(3)	C(29)–N(4)–Cu(2)	111.3(3)
C(10)–N(2)–Cu(1)	130.2(3)	C(27)–N(5)–Cu(2)	128.7(3)
C(11)–N(2)–Cu(1)	113.1(3)	C(28)–N(5)–Cu(2)	112.8(3)
C(14)–N(3)–Cu(1)	106.0(2)	C(31)–N(6)–Cu(2)	108.4(2)

Symmetry operations: a: x, $y-1$, $z+1$; b: x, $y+1$, $z-1$.

NBT (9.32×10^{-5} M), riboflavin (6.80×10^{-6} M), and tetramethyl-ethylenediamine (1.0×10^{-4} M) in phosphate buffer at pH 7.8, were used. The superoxide anion was enzymatically generated by the riboflavin system and spectrophotometrically detected by monitoring the formation of the reduced reporter molecule, which absorbs at 560 nm. The NBT reduction rate was measured in the presence and absence of SOD or the investigated complex for 210 s. All measurements were carried out at 25 ± 0.2°C using 1×1 cm thermostatted cuvettes. The IC_{50} (the concentration of SOD or the complex which causes 50% inhibition of NBT reduction) of SOD or the complex was calculated. Each final result for IC_{50} is the average of at least three independent determinations.

3. Results and discussion

The elemental analysis for the complex is in good agreement with the formula, $[Cu(H_2O)(L\text{-val})(phen)]Cl \cdot H_2O$. The complex is soluble in water and polar organic solvents such as methanol, ethanol, DMF and acetronitrile, but not in less polar organic solvents. Molar conductivity in ethanol shows a 1 : 1 electrolyte ($\Lambda = 46\ S\ cm^2\ mol^{-1}$) [14].

3.1. *Crystal structure*

Selected bond lengths and angles for the complex are given in table 3. Crystals of the complex are triclinic; space group $P1$ was chosen as the acid component used

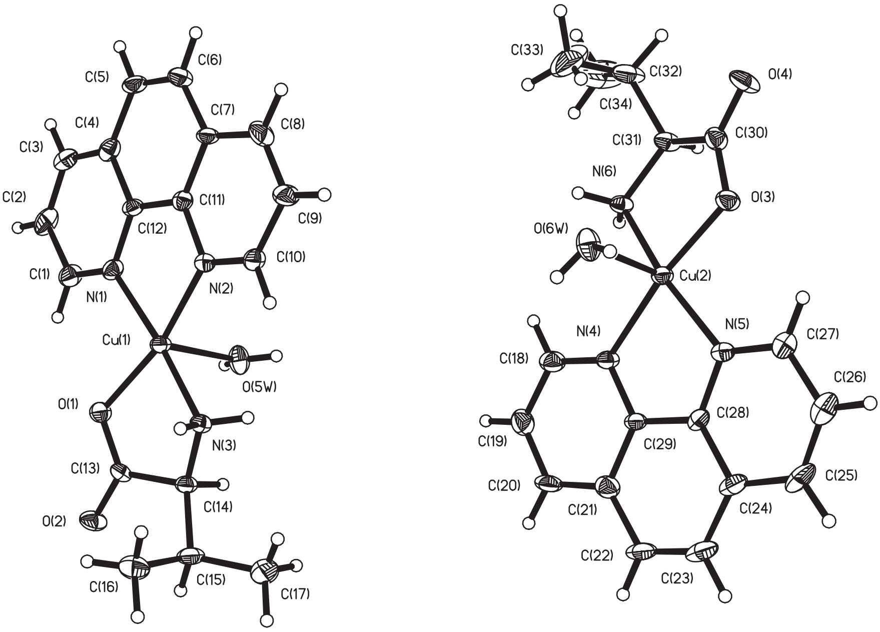

Figure 1. ORTEP plot showing the structure of two crystallographically independent molecules of $[Cu(H_2O)(L\text{-Val})(phen)]^+$. The chloride ion, crystal water molecule and hydrogen atoms were omitted for clarity.

was enantiopure (*L*)-valinate. The complex has crystallographically independent $[Cu(H_2O)(phen)(L\text{-Val})]^+$ subunits **Cu1** and **Cu2** in the unit cell, essentially diastereoisomers with each other. Each Cu(II) ion coordinates two nitrogen atoms of phen and the amino nitrogen and one carboxylate oxygen atoms of *L*-Val [Cu(1)–O(1) = 1.940(3), Cu(1)–N(1) = 2.011(4), Cu(1)–N(2) = 2.017(4), and Cu(1)–N(3) = 1.982(3) Å for complex **Cu1**, Cu(2)–O(3) = 1.909(3), Cu(2)–N(4) = 2.025(4), Cu(2)–N(5) = 2.000(4), and Cu(2)–N(6) = 1.996(3) Å for complex **Cu2**]; one water oxygen atom is axial [Cu(1)–O(5W) = 2.229(3) Å for complex **Cu1**, and Cu(2)–O(6W) = 2.237(3) Å for complex **Cu2**]. The resulting coordination geometries are distorted square-pyramidal (figure 1), where N(1), N(2), N(3), O(1) and Cu for complex **Cu1** deviate by −0.0467, 0.0505, 0.0469, −0.0507, and −0.1810 Å, respectively, from the least-squares plane ($66.875x - 1.501y - 0.171z = 0.9830$) defined by the four ligating atoms N(1), N(2), N(3), and O(1); N(4), N(5), N(6), O(3) and Cu atoms for complex **Cu2** deviate by −0.0212, 0.0887, 0.0871, −0.0255, and −0.1291 Å, respectively, from the least-squares plane ($6.561x - 3.269y - 0.647z = 4.9497$) defined by the four ligating atoms N(3), N(4), N(5), and O(3), indicating that the five atoms in equatorial positions are approximately coplanar. The bond angles observed around the central Cu range from 81.26(16) ~ 100.45(15)° in equatorial positions and from 88.44(14) ~ 98.96(14)° (apical positions), showing the angle variability in the geometry adopted by the five-coordinate Cu(II) complexes. The carboxyl group of the amino acid coordinates to Cu(II) *via* one oxygen atom as a unidentate group. Electron delocalization has been observed in the carboxyl group, but the bond distances [1.264(6) ~ 1.283(6) Å] between the coordinated oxygen atoms and the carbon atoms are slightly longer than those

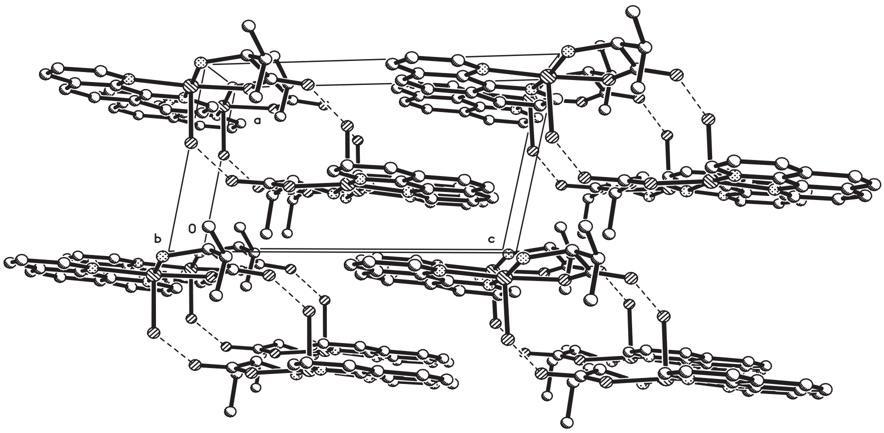

Figure 2. The crystal packing view of the complex.

[1.211(6) ~ 1.245(6) Å] between the uncoordinated oxygen atoms and the carbon atoms as expected. The molecular structures exhibit significant asymmetry.

Cu1 and Cu(2) are linked by a complex network of hydrogen bonds [O(6W) ··· O(2) in 2.745(5) Å in x, $y-1$, $z+1$, O(5W) ··· O(4b) = 2.696 Å in x, $y+1$, $z-1$] and phen-ring stacking interactions (the average distances between neighboring phenanthroline rings are 3.43 and 3.47 Å) (figure 2), which are of the same -a-b-a-b- type observed in the complex [Cu(H_2O)(*L*-glu)(phen)] · $3H_2O$ [15]. This stacking interaction is similar to the stacking interaction between neighboring DNA bases in the direction of the molecular axis in the DNA double helix.

3.2. *Infrared absorption spectrum*

The IR spectrum provides further evidence for the molecular structure of the complex. The strong and broad band at 3407 cm^{-1} is most likely the stretching vibrations of the coordinated and crystal water molecules. The group of bands appearing at 3133 and 2956 cm^{-1} can be attributed to the stretching vibrations of coordinated NH_2. The absence of any band in the region 1750 ~ 1700 cm^{-1} in the IR spectrum of the isolated complex suggests the coordination of the COO^- group of *L*-Val to the central Cu(II). The bands at 1643 and 1389 cm^{-1} can be attributed, respectively, to the antisymmetric and symmetric stretching vibrations of the coordinated carboxylate. The value of $\Delta\nu_{\mathrm{Co_2}}$ ($\Delta\nu^{as}_{\mathrm{Co_2}} - \nu^{s}_{\mathrm{Co_2}} = 254\,\mathrm{cm}^{-1}$) is consistent with monodentate coordination of the carboxylate group [15]. Thus, the monovalent anion of *L*-Val is coordinated to the metal ion as a N,O-bidentate ligand, in agreement with the result obtained by X-ray diffraction. The band at 1601 cm^{-1} is most likely assigned to the stretching vibration of the C=N group of the phen ligand and confirms its coordination to the metal ion [16]; alternatively, this band could be ascribed to the deformation mode δ_{NH} of the N–H group belonging to the amino acid moiety [17].

3.3. *Electronic absorption spectrum*

The electronic absorption spectrum of the title complex in the ethanol solution presents four important absorption bands. The strong bands at 213, 255 and 272 nm can be attributed to the $\pi \rightarrow \pi^*$ transitions of the phen ligand and the broad and weak absorption band at 610 nm to the d → d transition of the central Cu^{2+} ion, consistent with related aromatic diamine-Cu^{2+}–amino acid complexes [18–24].

3.4. *Thermal analysis*

In order to investigate the thermal stability of the complex, a TG-DTG study of the title complex was performed in the range of 23 ~ 470°C. The first weight loss (8.32%) occurs between 81.9 ~ 123.8°C (one peak at 81.9°C in DTG), corresponding to the loss of crystalline and coordinated water molecules. The second weight loss (26.93%) occurs between 123.8 ~ 402°C (two strong peaks at 164.3 and 318.5°C in DTG), corresponding to the loss of the *L*-Val ligand. The phen ligand was lost slowly when the temperature was increased to 450°C showing strongly coordinating phen.

3.5. *SOD-like activity*

The superoxide dismutase activity of the complex has been measured by the photoreduction of nitroblue tetrazolium (NBT). In the presence of light and a suitable hydrogen donor (tetramethyl ethylenediamine), riboflavin generates $\overline{\mathrm{O}}_2^{\bullet}$, and NBT is reduced by $\overline{\mathrm{O}}_2^{\bullet}$, which results in a linear accumulation of blue formazan and an increase in the absorbance at 560 nm. When SOD or a model compound (MSOD) is present, the spontaneous dismutation of $\overline{\mathrm{O}}_2^{\bullet}$ is negligible. In figure 3, absorbance values as a function of time are plotted as a good straight line and the slopes of the linear regression curves decrease with increase of the concentration of the complex, indicating that:

$$\eta \text{ (\% inhibition of NBT reduction)} = (1 - k'/k) \times 100\% \tag{1}$$

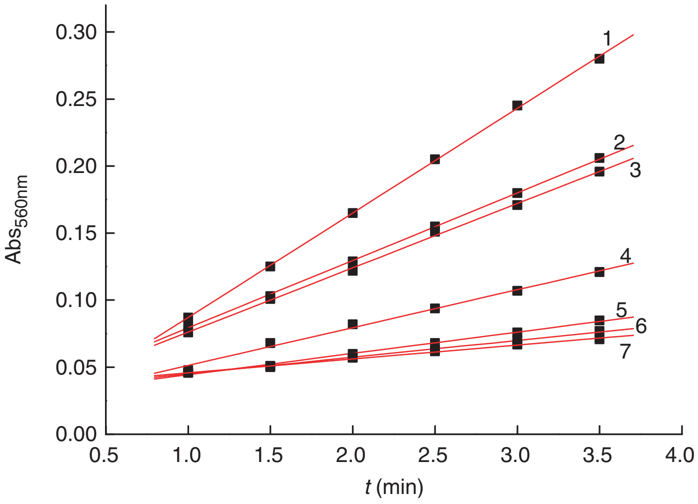

Figure 3. Absorbance values (Abs_{500}) as a function of time (t) plotted in a range in which a good straight line is observed [complex/M: (1) 0 (in absence of the complex), (2) 8×10^{-8}, (3) 1×10^{-7}, (4) 4×10^{-7}, (5) 6×10^{-7}, (6) 8×10^{-7} and (7) 1×10^{-6}].

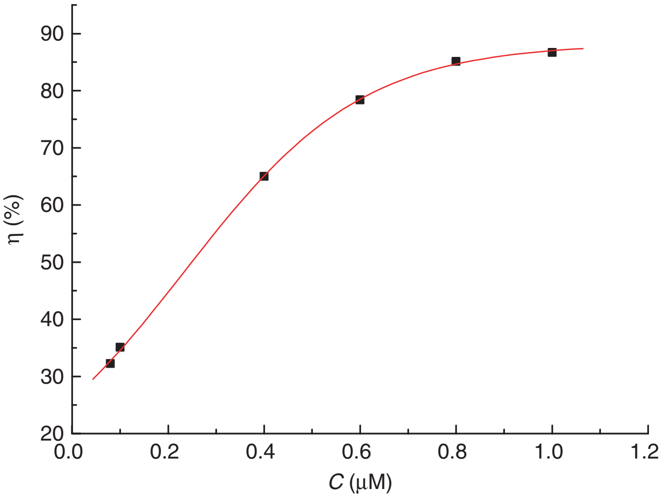

Figure 4. A plot of percentage of inhibiting NBT reduction with an increase in the concentration of the complex.

Table 4. SOD-like activities described by IC_{50} for copper(II) complexes.

Complex	$IC_{50} = \mu M$	Reference
Native CuZnSOD	0.0147	This work
$[Cu(H_2O)(L\text{-Val})(phen)]Cl \cdot H_2O$	0.248	This work
$[(tren)Cu(E\text{-}ImH)](ClO_4)_2$	175	[25]
$Cu(amino\ acid)_2$	0.3 ~ 6	[26]
$[CuL_2(4\text{-}mHim)_2]$	5.86	[27]

where k' and k present the slopes of the straight line of absorbance values as a function of time in the presence and absense of SOD or a model compound, respectively. Figure 4 shows percentage inhibition of the reduction of nitrobluetetrazolium plotted against the concentration of the complex.

The SOD-like activity of a model compound is usually defined as one unit SOD activity, which is the concentration of a model compound or enzyme, which causes 50% inhibition reduction of NBT. The more efficient a model compound, the lower the concentration that corresponds to 50% inhibiton of NBT or reduction the IC_{50} value. The IC_{50} values of the complex and the corresponding copper(II) complexes [25–27] are presented in table 4. The complex tested in this work has the highest SOD-like activity, which could be related to the distorted square-pyramidal geometry of the complex, with fast exchange of water molecules weakly linked to the center copper(II), and the coordination site belonging to nitrogen heteroatomic rings such as pyridines important for a high SOD activity [27, 28]; the lower activity of complexes $[CuL_2(4\text{-}mHim)_2]$ and $Cu(amino\ acid)_2$ compared with complex $[Cu(H_2O)(L\text{-Val})(phen)]Cl \cdot H_2O$ could be correlated with the strong field experienced by the Cu(II) in square-planar geometry, preventing the interaction of the complexes with superoxide radical, disfavoring formation of the intermediate copper-superoxide adduct [27]; the highest IC_{50} value and therefore the lowest SOD activity for $[(tren)Cu(E\text{-}ImH)](ClO_4)_2$ could be mainly attributed to the trigonal bipyramidal geometry of the complex and stronger coordination of E-ImH to central copper ion in comparison to water, disfavoring approach of the superoxide anion and geometrical change of the copper complexes, which is essential for the catalysis as the geometry of copper(II) in SOD changes from distorted square pyramidal to distorted tetrahedral copper(I) during catalysis [5, 25].

Though the activity of $[Cu(H_2O)(L\text{-}Val)(phen)]Cl \cdot H_2O$ is about 17 times less than that of the native Cu, Zn-SOD, the complex is a potent SOD mimic considering the very low molecular weight of the complex when compared with that of the native SOD enzyme (MW 32000 D).

Supplementary data

Crystallographic data in CIF format are been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material No. 267641 and can be obtained by contacting the CCDC.

Acknowledgement

This work was supported by the Natural Science Foundation of Guangdong Province (No. 04105986).

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