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ORIGINAL PAPER

Synthesis, crystal structure, electrochemical property, and antioxidant activity of copper(II) complex based on 4-butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine

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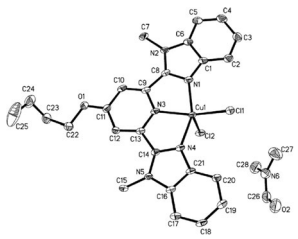
Abstract A new copper(II) complex $[Cu(bmbp)Cl_2]\cdot DMF$, where bmbp is 4-butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine, was synthesized and characterized by X-ray single-crystal structure analysis. The complex crystallizes in triclinic, space group P-1 with $a = 8.4551(3)$ Å, $b = 12.8262(4)$ Å, $c = 14.7111(5)$ Å, $\alpha = 64.335(3)°$, $\beta = 75.314(3)°$, $\gamma = 86.749(2)°$, $V = 1388.42(8)$ Å^3, $Z = 2$. The Cu(II) ion adopts a distorted trigonal bipyramidal geometry coordinated by three nitrogen atoms of the ligand and two chloride atoms. TG analysis showed that the complex has high thermal stability. Electrochemical measuring exhibited an irreversible one-electron transfer process. DPPH radical scavenging assay showed that the ligand and its Cu(II) complex exhibited much lower antioxidant activity than that of ascorbic acid.

Graphical abstract



Keywords Benzimidazole · Copper(II) complex · Crystal structure · Electrochemical property · Antioxidant activity

Introduction

Benzimidazole derivatives which are an important class of nitrogen-containing heterocyclic compounds, have a wide range of applications in medicinal chemistry, coordination chemistry, photochemistry, and bioinorganic chemistry [1–4]. Recently, more and more people have shown great interest in the study of benzimidazole derivatives because of their important biological and pharmic activities, including antibacterial [5], antiviral [6], antioxidant [7], anti-HIV [8], and anticancer [9, 10].

In our recent study, some benzimidazole derivatives and their metal complexes have been synthesized and evaluated for their fluorescence properties and in vitro anticancer activities [11–13]. Among these complexes, copper(II) complexes have received little attention. As we know, copper is an essential trace element for human body, and is required for normal cellular activity as a cofactor for many enzymes. Many copper(II) complexes have been found with different pharmacological effects such as anti-proliferative, anti-cancerous, anti-bacterial, nuclease mimetic and SOD mimetic properties [14]. In addition, some of them have shown radical scavenging properties also. Antioxidant activity, especially free radical scavenging activity, has a great importance due to the deleterious role of free radicals in foods and in biological systems. Free radicals formed in biological systems may damage the biomolecules of living cells and break the DNA strands, which cause a number of human diseases and cancers [15].

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Herein, we synthesized a mononuclear copper(II) complex obtained with tridentate NNN-donor ligand 4-butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine (bmbp). The electrochemical property of copper(II) complex was investigated by cyclic voltammetry. Besides, antioxidant activities against DPPH radical were assessed in vitro.

Results and discussion

Synthesis and characterization

As shown in Fig. 1, the synthesis of ligand started with chelidamic acid which was heated with *N*-methyl-1,2-phenylenediamine in phosphoric acid (85 %) at 180 °C for 10 h to afford 2,6-bis(1-methyl-2-benzimidazolyl)pyridin-4-ol (**1**). Then it was reacted with *n*-butyl bromide in dry K_2CO_3/DMF system under nitrogen atmosphere to yield the ligand 4-butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine (**2**). The ligand coordinates easily with $CuCl_2{\cdot}2H_2O$ to form the copper(II) complex **3**. These synthesized compounds were characterized and confirmed by IR spectroscopy, ^{1}H NMR, ^{13}C NMR, and ESI mass spectrometry (Supplementary Figs. S1–S7). In the ^{1}H NMR spectrum of the ligand, the signals of $\delta = 7.95$, 7.47, 7.37, and 7.86 ppm are from phenyl rings and pyridine ring hydrogen atoms. The peaks at 1.86, 1.54, 1.27, and 1.00 ppm are attributed to four hydrogen atoms of $-CH_2-$ and $-CH_3$. The $-CH_3$ proton attached to N atom is seen as a singlet at 4.25 ppm. The H atoms signals of the ligand are all in good agreement with the assumed structure.

IR spectra and thermal analysis

The IR spectra of the copper(II) complex was very similar to the free ligand (Fig. S1), except some slight shifts of a few vibration bands caused by copper ions. In the IR spectra, the free ligand shows the weak bands in the region 2951–2867 cm^{-1} due to $-CH_3$ and $-CH_2$ stretching vibrations. The medium bands around 1036 cm^{-1} are attributed to the ν(C–O) vibrations. The aromatic ν(C=C) stretching vibrations are observed in the range 1470–1483 cm^{-1}. The C–H bendings of benzimidazole ring appear around 743 cm^{-1} as strong bands. The C–N vibrations appearing at 1411 cm^{-1} in the spectra of the free ligand are shifted to lower wavenumbers at 1400 cm^{-1} in that of complex. The C=N stretching frequencies can be found at 1590 cm^{-1} in ligand, while the C=N stretching vibrations of the complex shifted toward high frequencies at 1606 cm^{-1}, which are blue-shifted compared to that of the ligand, indicating that the nitrogen atoms of the ligand are coordinated to the copper(II) ions.

The thermogravimetric analysis (TGA) of the title complex was carried out from 30 to 700 °C under a nitrogen atmosphere at a heating rate of 10 °C/min, as shown in Fig. 2. TG curve indicates that the complex is stable up to 265 °C. The first weight loss from 265 to 288 °C is related to the release of one DMF molecules (observed 13.88 %, calculated 11.81 %). Then when the temperature above 360 °C, the complex structure begins a slow weight loss process which is due to the decomposition of organic units. TG analysis shows that the complex has a good thermal stability.

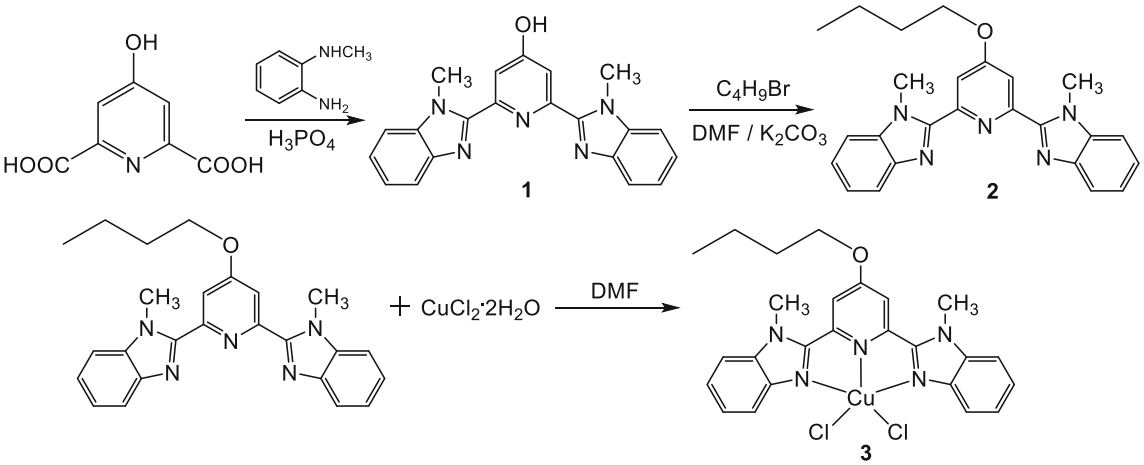

Fig. 1 The synthesis route of the ligand and the complex

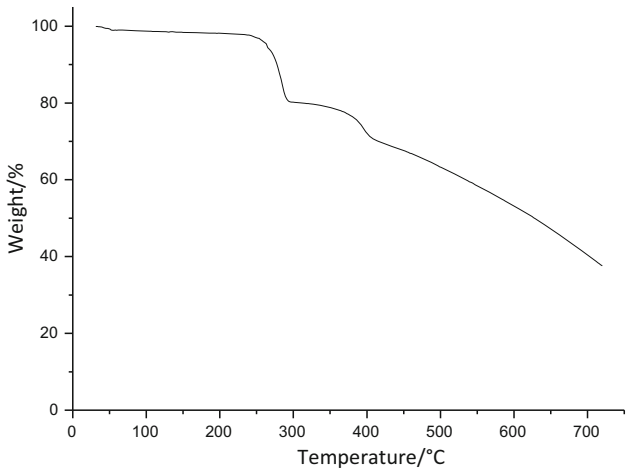

Fig. 2 TG curve of the title complex

Structure analysis

The ORTEP drawing of the complex is shown in Fig. 3. The selected bond lengths and bond angles are listed in Table 1. The complex is a five-coordinated mononuclear copper(II) complex in which the central copper ion is chelated by one neutral ligand and coordinated to two chloride ions. One uncoordinated DMF molecule is present in the molecular structure. As shown in Table 1, the bond lengths of Cu(1)–N(1), Cu(1)–N(4), and Cu(1)–N(3) are respectively 2.021(2), 2.019(2), and 2.013(2) Å, which are located in the range observed compared with other Cu(II) complexes [16]. The bond lengths of Cu(1)–Cl(1) 2.2742(8) Å is shorther than that of Cu(1)–Cl(2) 2.4327(8) Å by 0.1585 Å. The bond angles of N(3)–Cu(1)–N(4), N(3)–Cu(1)–N(1), N(3)–Cu(1)–Cl(1), N(3)–Cu(1)–Cl(2) are 77.72(9)°, 78.21(9)°, 149.87(7)°, and 101.23(7)°, respectively. The structure adopts a distorted trigonal bipyramidal geometry as indicated by the value of the trigonal index parameter $\tau = (\alpha - \beta)/60 = 0.69$, where α(N3–Cu1–Cl1) = 149.98° and β(Cl1–Cu1–Cl2) = 108.87° ($\tau = 0$ is for a perfect square pyramidal geometry and $\tau = 1$ is for a regular trigonal bipyramidal geometry [17]). The chloride ions Cl(1) and Cl(2) and pyridine nitrogen atom N(3) occupy the equatorial positions whereas benzimidazole imine nitrogen atoms N(1) and N(4) are placed in an axial positions. The two benzimidazole rings and the pyridine ring in the ligand are nearly in the same plane, similar to those reported benzimidazole complexes [18, 19].

In the crystal structure, as shown in Fig. 4, the benzimidazole rings from the adjacent units arrange in an offset face-to-face fashion by $\pi\cdots\pi$ stacking. The geometrical parameters describing the π-stacking are listed in Table 2. Here X is the distance between the centroids of the stacked aromatic rings, d is the perpendicular distance between their mean planes, δ is the offset between the centres measured along one of the planes, α is the angle between the line connecting centroids (X) and the normal to the plane of aromatic system (d), and β is the dihedral angle between the subsequent planes in a stack, according to Fig. S8. The $\pi\cdots\pi$ stacking interactions lead the complex to a 1D chain. The neighboring chains are further extended into a 2D layers through weak C–H···Cl and C–H···O intermolecular hydrogen bonds interactions between

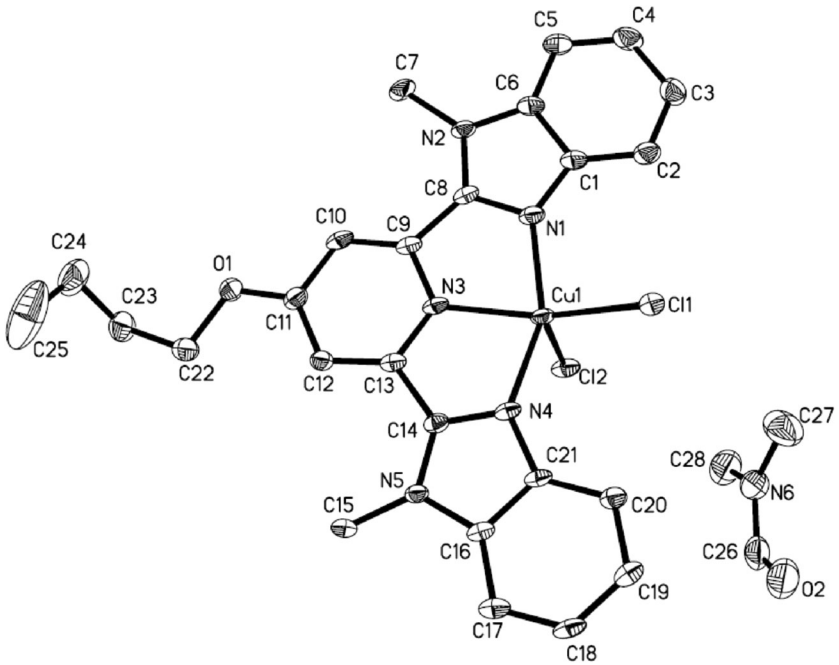

Fig. 3 ORTEP view with 50 % probability level of the complex (H atoms are omitted for clarity)

Table 1 Selected bond lengths and bond angles for complex

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Cu(1)–N(1)	2.021(2)	Cu(1)–N(3)	2.013(2)	Cu(1)–N(4)	2.019(2)
Cu(1)–Cl(1)	2.2742(8)	Cu(1)–Cl(2)	2.4327(8)		
Angle	*ω*/deg	Angle	*ω*/deg	Angle	*ω*/deg
N(3)–Cu(1)–N(4)	77.72(9)	N(3)–Cu(1)–N(1)	78.21(9)	N(4)–Cu(1)–N(1)	154.63(10)
N(3)–Cu(1)–Cl(1)	149.87(7)	N(3)–Cu(1)–Cl(2)	101.23(7)	N(1)–Cu(1)–Cl(1)	98.28(7)
N(1)–Cu(1)–Cl(2)	98.57(7)	N(4)–Cu(1)–Cl(1)	98.47(7)	N(4)–Cu(1)–Cl(2)	93.87(7)
Cl(1)–Cu(1)–Cl(2)	108.87(3)				

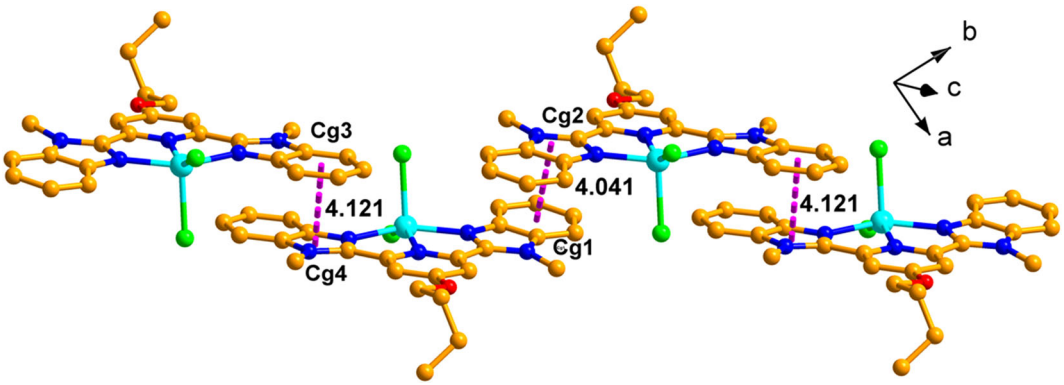

Fig. 4 View of the 1D chain generated by the π···π interactions in the complex (H atoms and DMF molecules are omitted for clarity)

Table 2 Geometrical parameters describing the π-stacking of the planar aromatic fragments

π···π stacking	*X*/Å	*d*/Å	*δ*/Å	*α*/°	*β*/°
Cg1···Cg2	4.041	3.548	1.92	28.41	0
Cg3···Cg4	4.121	3.397	2.34	34.58	0

Cg1 = C1–C2–C3–C4–C5–C6; Cg2 = C1–C6–N2–C8–N1; Cg3 = C16–C17–C18–C19–C20–C21; Cg4 = C16–C21–N4–C14–N5

benzimidazole ring, chloride anions and DMF molecule in adjacent chains. The DMF molecular is involved in hydrogen bonds connecting the chains to give a 2D structure (Fig. 5). The C(3)–H(3A)···O(2) hydrogen bonds (C–O 3.303 Å and C–H–O 156°), the C(28)–H(28C)···Cl(2) hydrogen bonds (C–Cl 3.760 Å and C–H–Cl 166°) contribute to the crystal packing, helping to stabilize the crystal structure.

Electrochemical properties

The redox properties of the Cu(II) complex were determined by cyclic voltammetry in DMF solution (1×10^{-3} mol dm^{-3}) containing 0.1 mol dm^{-3} $Bu_4N{\cdot}ClO_4$ at room temperature under air atmosphere at the scan rate of 25 to 200 mV/s. All potentials are referred to the Ag/AgCl reference. The cyclic voltammogram scanning from −0.2 to 0.8 V is shown in Fig. 6. The Cu(II) complex exhibits a pair of cathodic and anodic peaks with $E_{pc} = -0.010$ V ($I_{pc} = -9.96 \times 10^{-6}$ A) and $E_{pa} = 0.532$ V ($I_{pa} = 5.73 \times 10^{-6}$ A) at scan rate of 100 mV/s. The separation between the cathodic and anodic peak potentials $\Delta E_p = 0.542$ V, the formal potential $E_{1/2} = (E_{pc} + E_{pa})/2 = 0.261$ V and the ratio of anodic/cathodic peak current $I_{pa}/I_{pc} = 0.575$ indicate that the electron transfer process of the complex is irreversible assignable to the Cu^{II}/Cu^{I} couple [20]. Additionally, in the scan rate range of 25–200 mV/s, the ΔE_p increases with scan rate from 0.491 V at 25 mV s^{-1}

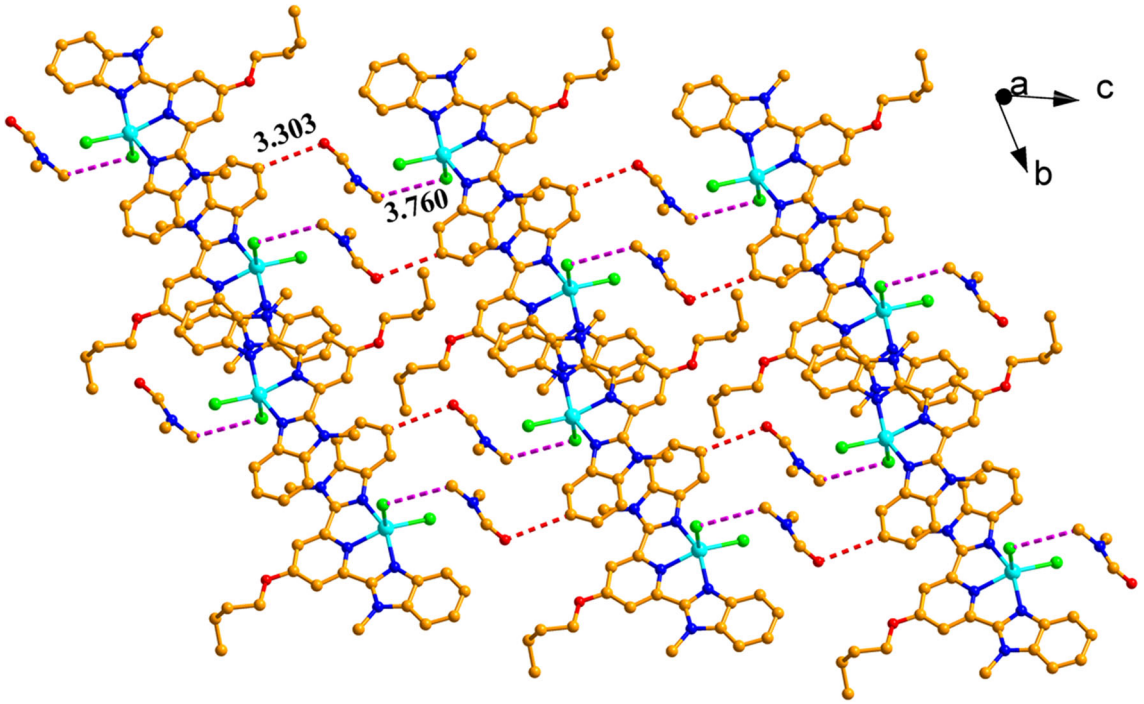

Fig. 5 View of the 2D layer connected by hydrogen bonds in the complex

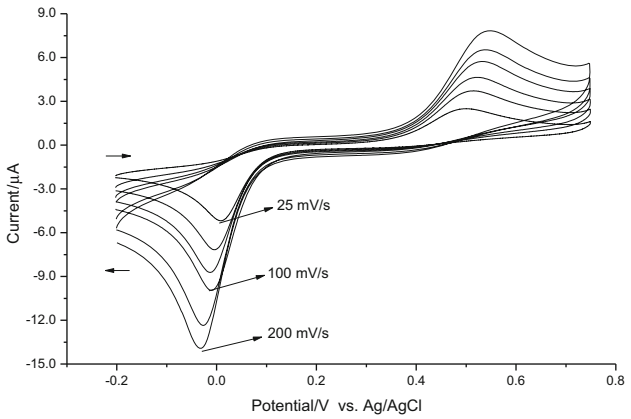

Fig. 6 Cyclic voltammogram of the title complex in DMF containing 0.1 mol dm^{-3} $Bu_4N{\cdot}ClO_4$ at scan rates of 25, 50, 75, 100, 150, and 200 mV s^{-1}

to 0.581 V at 200 mV s^{-1}, while a shift of the E_{pc} from 0.008 to −0.033 V is observed. The ratio between the cathodic peak current and the square root of the scan rate ($I_{pc}/v^{1/2}$) is approximately constant. From this cyclic voltammetry data it can be deduced that the redox couples are related to an irreversible one-electron transfer process.

Antioxidant activity

The model of scavenging the stable DPPH radical is a widely used method to evaluate antioxidant activities in a relatively short time in comparison with the other methods. DPPH is a stable free radical and accepts an electron or hydrogen radical to become a stable diamagnetic molecule [21]. The reduction capability of DPPH radicals can be determined by a decrease in their absorbance at 517 nm. The decrease in absorbance of DPPH radical was caused by antioxidants because of the reaction between antioxidant molecules and radical progresses, which results in the scavenging of the radical by hydrogen donation. It is visually noticeable as a discolouration from purple to yellow [22]. Hence, $DPPH^{\cdot}$ scavenging method is usually used to evaluate the antioxidant activity of antioxidants.

The antioxidant activity against $DPPH^{\cdot}$ radical of the ligand and corresponding Cu(II) complex were investigated and compared to ascorbic acid. The results were shown in Fig. 7. The scavenging activity increased with increasing concentration of the tested substances. From these curves, the 50 % inhibitory concentration (IC_{50}) values could be determined. It was observed that, the IC_{50} value of ligand and complex against $DPPH^{\cdot}$ radical is 256 and 177 μM, respectively. They all exhibited much lower ability to scavenge $DPPH^{\cdot}$ radical than that of ascorbic acid (83 μM).

The antioxidant kinetics of tested compounds were studied by monitoring the decay of the absorbance peak of DPPH at 517 nm over time. As seen in Fig. 8, ascorbic acid reacted rapidly with DPPH radical reaching a steady state after 5 min. For the ligand and its complex, the steady state was reached after approximately 45 and 40 min,

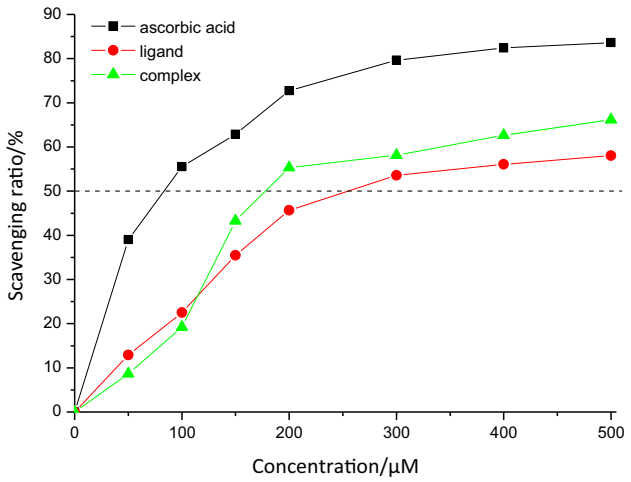

Fig. 7 Scavenging activity of the ligand and complex on DPPH radical

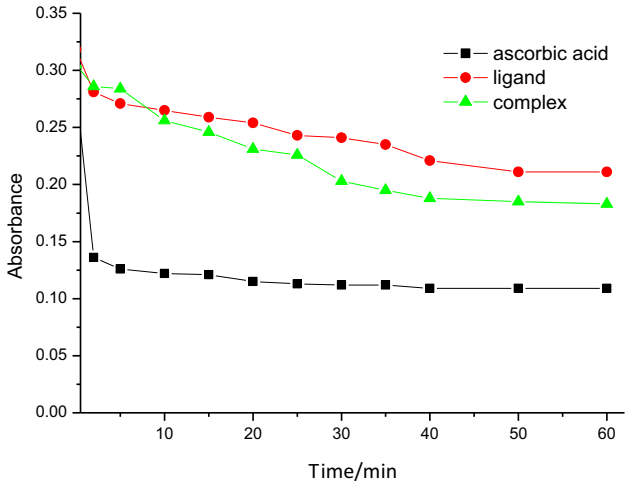

Fig. 8 Decay of DPPH (0.05 mM) absorbance at 517 nm for tested compounds (0.20 mM)

respectively. These kinetic curves showed that the ligand and its complex reacted with DPPH radicals much slower than ascorbic acid, since these compounds lack hydroxyl groups which favor the H-donating activity leading to the formation of the non-radical form, DPPH–H. Therefore, it is concluded that DPPH radicals react with the compounds might be due to the electron transfer from compound to the DPPH radical.

Conclusions

A new mononuclear copper(II) complex $[Cu(bmbp)Cl_2]$·DMF, based on 4-butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine (bmbp) was synthesized and characterized by X-ray single crystal structure analysis. In the complex, the copper ion distorted trigonal bipyramidal geometry is coordinated by three nitrogen atoms of the ligand and two chloride ions. The CV results of the complex exhibited an irreversible one-electron transfer process. Moreover, the ligand and its Cu(II) complex exhibited much lower antioxidant activity against DPPH radical than that of ascorbic acid.

Experimental

Chelidamic acid, *N*-methyl-*o*-phenylenediamine dihydrochloride, *n*-butyl bromide, phosphoric acid, and 1,1-diphenyl-2-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich. All the chemicals and solvents used were of analytical grade and without further purification. ^{1}H NMR and ^{13}C NMR spectroscopic measurements were carried out on a Bruker DRX-400 NMR spectrometer,using TMS ($SiMe_4$) as an internal reference. The solid infrared spectra (IR) were obtained from a Bruker Nicolet 6700 FT-IR spectrometer using KBr pellets. Mass spectra were obtained on a Bruker amaZon SL spectrometer using electrospray ionization(ESI). Thermogravimetric analysis (TG) was performed under N_2 atmosphere at a heating rate of 10 °C/min on a Perkin Elmer STA6000 thermal analyzer. The cyclic voltammetric (CV) measurements were performed using a CHI660B electrochemical workstation connected with a three-electrode system: a 0.10 cm diameter Glassy carbon (GC) disc as working electrode, an Ag/AgCl electrode as reference electrode, a Pt wire as auxiliary electrode and 0.1 mol dm^{-3} $Bu_4N{\cdot}ClO_4$ solution as supporting electrolyte. The DPPH radical scavenging activity was carried out with 722 UV–Vis spectrophotometer.

2,6-Bis(1-methyl-2-benzimidazolyl)pyridine-4-ol (**1**, $C_{21}H_{17}N_5O$)

A mixture of 2.00 g chelidamic acid (10 mmol), 4.10 g *N*-methyl-*o*-phenylenediamine dihydrochloride (21 mmol), and 10 cm^3 phosphoric acid (85 %) were heated to 180 °C and stirred for 10 h. The dark blue liquid was poured into 200 cm^3 of distilled water, and the pH was adjusted to 7–8 by adding ammonium hydroxide (15 %). The precipitate was filtered, washed well with water and recrystallized from methanol to give white prisms. Yield: 2.77 g (78 %); m.p.: 286.2–288.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 11.38$ (s, 1H), 7.79 (s, 2H), 7.76 (d, $J = 7.7$ Hz, 2H), 7.68 (d, $J = 7.9$ Hz, 2H), 7.39–7.28 (m, 4H), 4.25 (s, 6H) ppm; ^{13}C NMR (101 MHz, DMSO-d_6): $\delta = 165.64$, 151.43, 150.35, 142.45, 137.54, 123.64, 122.88, 119.92, 111.33, 33.02 ppm; IR (KBr): $\bar{\nu} = 3394$,

3040, 2734, 1602, 1560, 1521, 1476, 1458, 1194, 1029, 747 cm^{-1}.

4-Butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine (**2**, $C_{25}H_{25}N_5O$)

A solution of 1.06 g 2,6-bis(1-methyl-2-benzimidazolyl)pyridine-4-ol (**1**, 3 mmol) in 30 cm^3 dry DMF was stirred with 2.07 g dry K_2CO_3 (5 equiv, 15 mmol) at 80 °C for 0.5 h under nitrogen. Then 0.38 cm^3 *n*-butyl bromide (3.5 mmol) was added dropwise and reacted for 5 h. After it was cooled, water was added and stirred until total K_2CO_3 dissolved. The precipitate was filtered and recrystallized in CH_2Cl_2/EtOH (1:1) to get white solid as the ligand bmbp. Yield: 0.91 g (74 %); m.p.: 258.6–259.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.95$ (s, 2H), 7.86 (d, 2H), 7.47 (d, 2H), 7.37 (s, 4H), 4.25 (s, 6H), 1.86 (s, 2H), 1.54 (m, 2H), 1.27 (d, 2H), 1.00 (t, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 166.65$, 151.03, 150.44, 142.48, 137.19, 123.50, 122.77, 120.12, 111.79, 109.90, 68.38, 32.52, 30.89, 19.09, 13.75 ppm; IR (KBr): $\bar{\nu} = 3096$, 2951, 2927, 2867, 1590, 1567, 1483, 1470, 1441, 1411, 1326, 1036, 1013, 865, 743 cm^{-1}; ESI–MS: $m/z = 434.2$ ([M + 23]).

4-Butyloxy-2,6-bis(1-methyl-2-benzimidazolyl)pyridine copper(II) chloride dimethylformamide monosolvate, [Cu(bmbp)Cl$_2$] DMF (**3**, $C_{28}H_{32}Cl_2CuN_6O_2$)

To a solution of 823 mg of the ligand bmbp (**2**, 2.0 mmol) in 20 cm^3 DMF was added 341 mg $CuCl_2{\cdot}2H_2O$ (2.0 mmol) and the resulting green solution was stirred for 30 min at room temperature. Then it was filtered and the filtrate was allowed to stand at room temperature for 1 week. Green block crystals of the title complex **3** were obtained. Yield: 881 mg (71 %); IR (KBr): $\bar{\nu} = 3482$, 3061, 2958, 2930, 2872, 1606, 1565, 1492, 1477, 1400, 1320, 1186, 1028, 855, 754 cm^{-1}. ESI–MS: $m/z = 509.1$ ([M-35]).

Structure determination

Crystallographic data of the title complex was collected at 150 K on Bruker CCD diffractometers equipped with a graphite-monochromatic Cu-Kα radiation ($\lambda = 1.54178$ Å). Crystals with suitable sizes (0.25 mm × 0.23 mm × 0.20 mm) were selected for data collection. The structures were solved by direct methods with SHELXS-97 [23] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as riding method. Details of X-ray experiment and crystal data are summarized in Table 3.

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference number 1056054. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html. (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.uk.

Table 3 Crystal data and structure refinement for complex

Empirical formula	$CuC_{28}H_{32}Cl_2N_6O_2$
Formula weight	619.04
Crystal system	Triclinic
Space group	P-1
a/Å	8.4551(3)
b/Å	12.8262(4)
c/Å	14.7111(5)
α/°	64.335(3)
β/°	75.314(3)
γ/°	86.749(2)
V/Å^3	1388.42(8)
Z	2
D_c/g cm^{-3}	1.481
Absorption coefficient/mm^{-1}	3.188
F(000)	642
Crystal size/mm^3	0.25 × 0.23 × 0.20
Theta range for data collection	3.83 to 59.99
Limiting indices	$-9 \le h \le 9$, $-14 \le k \le 12$, $-16 \le l \le 12$
Reflections collected	6532
Independent reflections (R_{int})	4078 (0.0410)
Completeness to theta	98.5 %
Data/restraints/parameters	4078/0/352
Goodness-of-fit on F^2	1.098
Final *R* indices $I > 2\ \sigma(I)$	$R1 = 0.0479$, $wR2 = 0.1342$
R indices (all data)	$R1 = 0.0492$, $wR2 = 0.1368$
Largest diff. peak and hole/ *e* Å^{-3}	0.727 and −0.720

DPPH· scavenging assay

The DPPH· scavenging capacity was measured according to a modified method of Turkoglua et al. [25]. In brief, DPPH solution in ethanol (0.05 mM) was prepared and 2.0 cm^3 of this solution was added to 2.0 cm^3 of tested samples with various concentrations (50–500 μM in DMSO). The reaction mixture was vortexed and incubated for 1 h in the dark at room temperature. The absorbance was recorded at 517 nm by using UV–Vis spectrophotometer. All determinations were performed in triplicate. Ascorbic acid was used as a positive control. The scavenging rate of DPPH· was calculated by the following formula:

$$\text{Scavenging rate}/\% = [1 - (A_x - A_{x0})/A_0] \times 100$$

where A_x is the absorbance of DPPH solution and tested sample, A_{x0} is the absorbance of the blank with ethanol and tested sample, and A_0 is the absorbance of the control with ethanol and DPPH solution.

The 50 % inhibitory concentration (IC_{50}) values for the $DPPH^{\cdot}$ scavenging assays of the ligand and the complex were respectively calculated from the curves of the inhibition percentage against the concentration. Based on the IC_{50} values, the antioxidant kinetics of tested compounds were evaluated by determining the reduction in absorbance at 0 min, and different time intervals over a period of 60 min.

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References

1. Liu SG, Cao WQ, Yu LL, Zheng WJ, Li LL, Fan CD, Chen TF (2013) Dalton Trans 42:5932
2. Boca R, Baran P, Dlhán L, Sima J, Wiesinger G, Renz F, El-Ayaan U, Linert W (1997) Polyhedron 16:47
3. Tong YP, Zheng SL, Chen XM (2007) J Mol Struct 826:104
4. Joubert A, Sun XW, Johansson E, Bailly C, Mann J, Neidle S (2003) Biochemistry 42:5984
5. Halafi-Nezhad AK, Soltani Rad MN, Mohabatkar H, Asrari Z, Hemmateenejad B (2005) Bioorg Med Chem 13:1931
6. Komazin G, Ptak RG, Emmer BT, Townsend LB, Drach JC (2003) Nucleosides, Nucleotides Nucleic Acids 22:1725
7. Wu HL, Zhang YH, Zhang JW, Yang ZH, Chen CY, Peng HP, Wang F (2015) Transition Met Chem 40:145
8. Rao A, Chimirri A, Clercq ED, Monforte AM, Monfortea P, Pannecouque C, Zappalà M (2002) II Farmaco 57:819
9. Kumar D, Jacob MR, Reynolds MB, Kerwin SM (2002) Bioorg Med Chem 10:3997
10. Gellis A, Kovacic H, Boufatah N, Vanelle P (2008) Eur J Med Chem 43:1858
11. Pan RK, Liu SG, Wang SX, Li GB, Su WY, Huang QW, He YM (2015) Z Anorg Allg Chem 641:627
12. Xie Q, Liu SG, Li XL, You XZ (2014) Dalton Trans 43:6973
13. Li GB, Wang SX, Su WY, Pan RK, Liu KD, Liu SG (2014) Russ J Coord Chem 40:764
14. Rajalakshmi S, Kiran MS, Nair BU (2014) Eur J Med Chem 80:393
15. Bloknina O, Virolainen E, Fagerstedt KV (2003) Ann Bot Lond 91:179
16. You XL, Wei ZH (2014) Transition Met Chem 39:675
17. Addison AW, Rao TN, Reedijk J, van Rijn J, Verschoor GC (1984) J Chem Soc Dalton Trans (7):1349
18. Liu SG, Zuo JL, Li YZ, You XZ (2004) J Mol Struct 705:153
19. Liu SG, Zhang LP, Liu J, Su WY, Shi XB (2012) Spectrochim Acta A 97:464
20. Addison AW, Hendriks HMJ, Reedijk J, Thompson LK (1981) Inorg Chem 20:103
21. Talaz O, Gulcin I, Goksu S, Saracoglu N (2009) Bioorg Med Chem 17:6583
22. Karagoz Genc Z, Selcuk S, Sandal S, Colak N, Keser S, Sekerci M, Karatepe M (2014) Med Chem Res 23:2476
23. Sheldrick GM (1997) SHELXS-97, Program for the Solution of Crystal Structures. University of Göttingen, Göttingen, Germany
24. Sheldrick GM (1997) SHELXL-97, Program for the Refinement of Crystal Structures from Diffraction Data. University of Göttingen, Göttingen, Germany
25. Turkoglua A, Durub ME, Mercanc N, Kivrak I, Gezer K (2007) Food Chem 101:267