Synthesis and Structure of a Novel Copper(II) Dinuclear Complex with 4,4′-Dipyridyl as the Bridge

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With *N*,*N*′-bis(benzimidazol-2-yl-methyl)amine as the ligand, a novel Cu(II) dinuclear complex was synthesized as a mimetic compound of superoxide dismutase (SOD). The complex was characterized with element analysis, UV and IR spectra. The crystal structure was determined by using X-ray diffraction analysis. The crystal structure shows that Cu(II) and its coordinated atoms construct distorted octahedron configuration with oxygen atoms of $(ClO_4^-)_s$ in the axial directions. The coordinated cations are linked by $(ClO_4^-)_s$ to form nonplanar sheets. All sheets are linked together into three-dimensional network by the intermolecular hydrogen bonds. The result of the activity assay indicates that the complex does have certain biological activity.

Keywords *N*,*N*′-bis(benzimidazol-2-yl-methyl)amine, Cu(II), three-dimensional network complex, crystal structure, quantum chemistry computation, biological activity

Introduction

Superoxide dismutase (SOD) [EC 1.15.1.1] can catalyze the dismutation reaction of $O_2^{-\cdot}$ to molecular oxygen (O_2) and hydrogen peroxide (H_2O_2). SOD appears to play an important role in both the animal and plant kingdoms to eliminate $O_2^{-\cdot}$ and protect living organisms from toxicity of $O_2^{-\cdot}$. SOD is a metalloenzyme and occurs in a wide range of organisms. Three different types of SOD_S have been found so far: SOD_S containing both Cu and Zn (Cu, Zn-SOD_S), Mn(Mn-SOD_S) and Fe(Fe-SOD_S) as factors of SOD_S[1](the subscript means plural). How to use small molecular complexes as SOD models is the aim that people have been exploring and is a hot topic in research field of SOD mimetic chemistry today.[2-4]

We reported some crystal structures and biological activities of mononuclear and trinuclear complexes[5-8] on the research area of SOD mimetic compounds. In this paper the structure and biological activity of a novel dinuclear Cu(II) complex are reported.

Experimental

Element analysis, UV-vis and IR (KBr) spectra were obtained with Perkin-Elmer Chn Elemental Analyser, TU-1221 Ultraviolet Spectrometer and TJ270-30 Infrared Spectrometer.

Synthesis and characterization

Cu(II) *mononuclear complex* *o*-Phenylenediamine (0.2 mol) and iminodiacetic acid (0.1 mol) were dissolved in ethylene glycol and refluxed for 24 h with stirring. After cooling, 450 mL of distilled water was added and pink precipitate appeared. The precipitate was filtered and dried, then recrystallized from the mixed solution of acetone and water ($V:V=1:1$) to give white powder, *N*,*N*′-bis(benzimidazol-2-yl-methyl)amine containing five molecules of water ($L\cdot 5H_2O$), $C_{16}H_{15}N_5\cdot 5H_2O$, m.p. 249—250 ℃. $Cu(ClO_4)_2\cdot 6H_2O$ (0.01 mol) was dissolved in hot methanol, 0.01 mol of ligand L dissolved in hot methanol was added into the above solution with stirring for 8 h. After standing, concentrating and filtering, the crude product was recrystallized from methanol to afford blue powder, $Cu(L)\cdot(ClO_4)_2\cdot CH_3OH$. Anal. calcd: C 35.69, H 3.32, N 12.23; found C 35.63, H 3.15, N 11.98.

Cu(II) *dinuclear complex with 4,4′-dipyridyl as the bridge* $Cu(L)\cdot(ClO_4)_2\cdot CH_3OH$ blue powder (2 mmol) was dissolved in 10 mL of methanol, 1 mmol of 4,4′-dipyridyl (dipy) dissolved in 5 mL of methanol was added into the above solution, then refluxed with stirring for 1 h, the precipitate was removed by filtration and washed with methanol, and recrystallized from methanol to obtain blue crystals, $LCudipyCuL\cdot(ClO_4)_4\cdot H_2O$ ($C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$). Anal. calcd: C 40.24, H 3.19, N 13.41; found C 40.20, H 3.21, N 13.40. UV-vis

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(EtOH) λ_{max}: 277.70, 271.20, 240.70, 218.60 nm; IR (KBr) ν: 3160 (ν_{N-H}), 1614 ($\nu_{C=C}$), 1474 and 1452 [$\nu_{C=N(imidazolyl)}$], 1278 [$\nu_{C-N(imidazolyl)}$], 1384 [$\nu_{C-N(alkylamino)}$]. By means of pyrogallol autoxidation[5,9] the biological activity of the complex was measured and the value of its pI_{50} is 4.80.

X-Ray diffraction experiment and structure solution

The crystal size of LCudipyCuL·$(ClO_4)_4$·H_2O for diffraction experiment is 0.30 mm × 0.25 mm × 0.20 mm. A total of 11342 reflections were collected on a Brucker AXS Smart-1000 CCD diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) with ω and θ scan mode in the range of $1.71° \leqslant \theta \leqslant 25.07°$. All reflections were corrected by Lp factor. 7084 independent reflections with $I \geqslant 2\sigma(I)$ were used in the structure analysis and refinements. The crystallographic parameters are as follows: $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$, M_r = 1253.74, monoclinic, a = 2.771(4) nm, b = 0.9432(11) nm, c = 2.501(3) nm, β = 120.17(5)°, V = 5.652(13) nm^3, D_c = 1.473 Mg/m^3, Z = 4, $F(000)$ = 2552, μ = 1.017 mm^{-1}, space group *Cc*.

The structure was solved by direct method and fourier synthesis method. The positions of hydrogen atoms were determined theoretically. Full matrix least-squares refinements of nonhydrogen atoms with anisotropic thermal parameters and hydrogen atoms with isotropic thermal parameters converged to final R = 0.0661, wR = 0.1462, S = 0.971, $(\Delta/\sigma)_{max}$ = 0.075, $(\Delta\rho)_{max}$ = 683 e/nm^3, $(\Delta\rho)_{min}$ = − 456 e/nm^3. All variables in refinements were 673.

Quantum chemistry calculation

With the PentiumIV computer, we carried out the quantum chemistry calculation to the complex molecule at HF/LanL2DZ level using Gaussian 98 program. The atomic coordinates used in the calculation were obtained from the crystal structure data. The computation model is shown in Fig. 1. The data of 76 atoms, 784 basis functions, 2060 primary Gaussian functions, 285 alpha electrons and 284 beta electrons were included to perform the calculation.

Results and discussion

Description of the crystal structure

The atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 1, selected bond lengths and bond angles in Table 2 and intermolecular hydrogen bonds in Table 3. A perspective drawing and the crystal packing of the complex $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$ are shown in Fig. 1 and Fig. 2.

The repeat unit of the structure contains two L ligands, two Cu(II) ions, four ClO_4^-, one water and one dipy. Two nonprotonating N atoms and one alkylamino N atom from L and one N atom from dipy coordinate together to Cu(II) ion in the equatorial plane and two oxygen atoms of $(ClO_4^-)_s$ coordinate to Cu(II) on the two axial directions with a distorted octahedron geometry which is

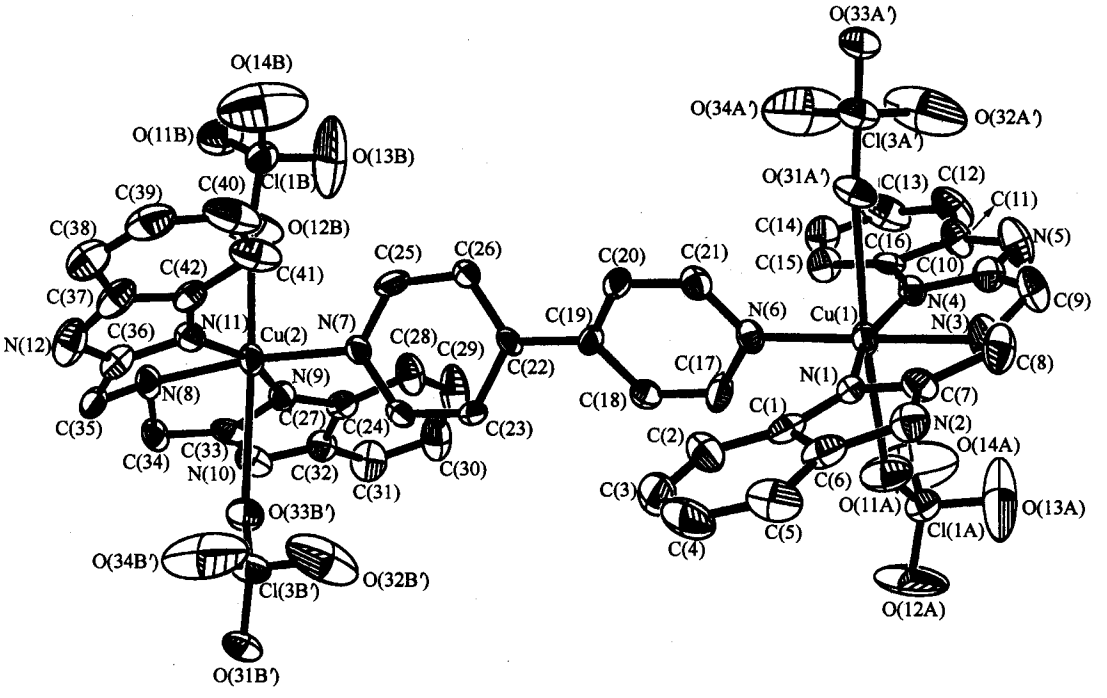

Fig. 1 A perspective drawing of the complex $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$.

Table 1 Non-hydrogen atomic coordinates and thermal parameters

Atoms	x	y	z	$U_{eq}{}^{a}$ ($\times 10^{-2}$ nm^2)
Cu(1)	0.2226(1)	−0.1079(1)	1.0297(1)	0.044(1)
Cu(2)	−0.0313(1)	0.3236(1)	0.5533(1)	0.047(1)
N(1)	0.2408(4)	−0.2841(10)	0.9995(4)	0.042(2)
N(2)	0.2759(4)	−0.5009(11)	1.0212(5)	0.059(3)
N(3)	0.2705(6)	−0.2060(10)	1.1124(5)	0.076(4)
N(4)	0.2177(4)	0.0388(10)	1.0841(4)	0.046(2)
N(5)	0.2360(6)	0.0966(12)	1.1787(6)	0.085(4)
N(6)	0.1748(4)	−0.0193(9)	0.9475(4)	0.042(2)
N(7)	0.0118(4)	0.2552(9)	0.6419(4)	0.042(2)
N(8)	−0.0661(4)	0.3993(10)	0.4640(4)	0.050(3)
N(9)	−0.0013(4)	0.5231(10)	0.5738(5)	0.050(2)
N(10)	0.0222(5)	0.7115(10)	0.5408(6)	0.061(3)
N(11)	−0.0641(4)	0.1430(11)	0.5084(5)	0.047(2)
N(12)	−0.1063(5)	0.0369(13)	0.4171(6)	0.078(4)
C(1)	0.2353(5)	−0.3429(13)	0.9447(7)	0.052(3)
C(2)	0.2167(6)	−0.2932(14)	0.8865(6)	0.065(4)
C(3)	0.2191(6)	−0.3718(17)	0.8440(7)	0.075(4)
C(4)	0.2410(7)	−0.5093(17)	0.8570(9)	0.087(5)
C(5)	0.2625(7)	−0.5663(16)	0.9147(9)	0.080(5)
C(6)	0.2589(5)	−0.4776(14)	0.9600(7)	0.061(4)
C(7)	0.2636(5)	−0.3807(13)	1.0423(6)	0.047(3)
C(8)	0.2766(6)	−0.3548(12)	1.1060(6)	0.068(4)
C(9)	0.2645(7)	−0.1462(12)	1.1604(6)	0.067(4)
C(10)	0.2404(6)	−0.0048(15)	1.1423(6)	0.058(3)
C(11)	0.2092(6)	0.2098(13)	1.1427(6)	0.060(4)
C(12)	0.1900(8)	0.3354(16)	1.1550(8)	0.085(5)
C(13)	0.1631(8)	0.4266(16)	1.1062(10)	0.090(6)
C(14)	0.1478(6)	0.3956(14)	1.0465(7)	0.068(4)
C(15)	0.1662(5)	0.2680(13)	1.0349(7)	0.058(4)
C(16)	0.1937(5)	0.1739(12)	1.0809(6)	0.042(3)
C(17)	0.1939(5)	0.0866(13)	0.9248(6)	0.064(4)
C(18)	0.1638(5)	0.1459(13)	0.8688(6)	0.054(3)
C(19)	0.1097(4)	0.1013(12)	0.8279(5)	0.041(3)
C(20)	0.0896(5)	−0.0097(13)	0.8487(5)	0.048(3)
C(21)	0.1223(5)	−0.0626(12)	0.9072(6)	0.049(3)
C(22)	0.0745(5)	0.1600(10)	0.7638(5)	0.038(3)
C(23)	0.0998(5)	0.2057(11)	0.7292(5)	0.045(3)
C(24)	0.0677(5)	0.2550(12)	0.6706(5)	0.048(3)
C(25)	−0.0115(5)	0.2156(13)	0.6748(6)	0.059(3)
C(26)	0.0166(5)	0.1659(13)	0.7352(5)	0.055(3)
C(27)	0.0295(5)	0.6153(12)	0.6237(6)	0.049(3)
C(28)	0.0420(6)	0.6010(14)	0.6859(6)	0.068(4)
C(29)	0.0723(8)	0.7076(17)	0.7249(7)	0.098(6)
C(30)	0.0922(8)	0.8252(19)	0.7058(8)	0.095(5)
C(31)	0.0748(6)	0.8385(14)	0.6425(8)	0.080(5)
C(32)	0.0440(5)	0.7300(14)	0.6023(6)	0.055(3)
C(33)	−0.0055(6)	0.5864(13)	0.5234(7)	0.056(4)

continued

Atoms	x	y	z	U_{eq}[a] ($\times 10^{-2}$ nm^2)
C(34)	-0.0350(5)	0.5197(13)	0.4617(6)	0.054(3)
C(35)	-0.0731(5)	0.2792(14)	0.4213(6)	0.060(4)
C(36)	-0.0810(5)	0.1519(14)	0.4484(7)	0.054(3)
C(37)	-0.1064(5)	-0.0635(15)	0.4601(8)	0.063(4)
C(38)	-0.1313(6)	-0.1958(16)	0.4467(9)	0.073(4)
C(39)	-0.1238(7)	-0.2570(20)	0.4976(11)	0.087(5)
C(40)	-0.0984(8)	-0.2000(20)	0.5571(11)	0.099(7)
C(41)	-0.0743(7)	-0.0622(15)	0.5699(8)	0.078(5)
C(42)	-0.0809(5)	0.0049(17)	0.5149(6)	0.063(4)
Cl(1)	0.3475(1)	0.1081(4)	0.0785(2)	0.061(1)
O(11)	0.3096(4)	0.0020(10)	0.0434(6)	0.093(3)
O(12)	0.3865(6)	0.1239(17)	0.0633(8)	0.179(8)
O(13)	0.3750(9)	0.0590(20)	0.1356(7)	0.222(9)
O(14)	0.3249(8)	0.2286(15)	0.0848(13)	0.230(11)
Cl(2)	0.2804(1)	0.0560(4)	0.8302(2)	0.062(1)
O(21)	0.3031(4)	0.0704(13)	0.8949(4)	0.103(4)
O(22)	0.3183(5)	-0.0097(15)	0.8172(5)	0.149(6)
O(23)	0.2719(8)	0.1903(13)	0.8057(8)	0.178(7)
O(24)	0.2296(6)	-0.0186(18)	0.8041(6)	0.176(7)
Cl(3)	0.0963(2)	0.8070(4)	0.0381(2)	0.061(1)
O(31)	0.1376(4)	0.7533(9)	0.0238(4)	0.067(2)
O(32)	0.1219(8)	0.8692(18)	0.0960(9)	0.196(9)
O(33)	0.0601(4)	0.6974(10)	0.0358(4)	0.074(3)
O(34)	0.0710(7)	0.9160(17)	0.0053(12)	0.233(12)
Cl(4)	0.9260(4)	0.1638(12)	0.2610(4)	0.245(5)
O(41)	0.8783(10)	0.1940(30)	0.2669(16)	0.367(18)
O(42)	0.9169(10)	0.440(20)	0.2205(10)	0.268(10)
O(43)	0.9656(9)	0.1030(30)	0.3197(8)	0.294(12)
O(44)	0.9127(13)	0.2810(20)	0.2205(12)	0.304(12)
O(51)	0.0141(7)	0.8273(13)	0.4285(7)	0.145(6)

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

stretched in the axial directions. The largest deviations of Cu(1) and Cu(2) from their equatorial planes are 0.00185 and 0.01070 nm respectively. This configuration is very similar to the CuZnCu trinuclear complex.[5] Cu(1) and Cu(2) are beyond the planes of four chelating rings [N(1)/C(7)/C(8)/N(3), N(4)/C(10)/C(9)/N(3) and N(8)/C(34)/C(33)/N(9), N(8)/C(35)/C(36)/N(11)] 0.04122, 0.03189 and 0.05527, 0.05208 nm. This shows that four chelating rings belong in envelope conformation. The dihedral angles between two benzimidazolyl planes are 5.81° [involving Cu(1)] and 5.96° [involving Cu(2)], the planar conformation of the ligand is similar to the reported structures.[4,5] The dihedral angle between two pyridyls of dipy is 32.50° smaller than 41.68° which is in uncoordinated dipy of the complex ($C_{37}H_{36}N_{12}O_7Zn$).[10] In the structure the dihedral angles between pyridyls and benzimidazolyls are in the range of 60.60°—77.94°.

The coordinated cations are linked by $(ClO_4^-)_s$ to form nonplanar sheets. A part of one sheet shows below: —Cu(2A)—O(33A)—Cl(3A)—O(31A)—Cu(1D)—O(11A)—Cl(1A)—O(12A)—Cu(2C)—O(33B)—Cl(3B)—O(31B)—Cu(1E)—O(11B)—Cl(1B)—O(12B)—Cu(2B)— (symmetry code : A x, y, z; B $1+x, y, z$; C $0.5+x, 0.5+y, z$; D $x, -y, z-0.5$; E $0.5+x, 0.5-y, 0.5+z$). All sheets are linked together into three-dimensional network by the intermolecular hydrogen bonds. From analysis above the existence of large space or channels is obvious (Fig. 2), this is the important micro structural environment for $O_2^{-\cdot}$ moving freely. Meanwhile Cu—O bond lengths are in the range of 0.2464—0.2786 nm, so these bonds evidently are weak. When $O_2^{-\cdot}$ attacks Cu(II), Cu—O bond will rupture easily and $O_2^{-\cdot}$ can coordinate to Cu(II) to form a new stronger bond. It can be seen that weak coordinated groups are also the important reason for this supermolecular compound with biological activity.

Table 2 Selected bond lengths (nm) and bong angles (°)

bond lengths (nm)			
Cu(1)—N(1)	0.1992(10)	Cu(1)—N(6)	0.1987(9)
Cu(1)—N(4)	0.1993(10)	Cu(1)—N(3)	0.2035(11)
Cu(1)—O(11A)	0.2484(10)	Cu(1)—O(31A′)	0.2634(10)
Cu(2)—N(11)	0.1992(11)	Cu(2)—N(9)	0.2016(11)
Cu(2)—N(7)	0.2023(9)	Cu(2)—N(8)	0.2065(10)
Cu(2)—O(12B)	0.2464(11)	Cu(2)—O(33B′)	0.2786(10)
bond angles (°)			
N(1)-Cu(1)-N(6)	97.1(4)	N(1)-Cu(1)-N(4)	162.8(4)
N(6)-Cu(1)-N(4)	100.2(4)	N(1)-Cu(1)-N(3)	81.1(4)
N(6)-Cu(1)-N(3)	177.8(5)	N(4)-Cu(1)-N(3)	81.6(4)
N(1)-Cu(1)-O(11A)	89.3(4)	N(3)-Cu(1)-O(11A)	87.6(4)
N(4)-Cu(1)-O(11A)	90.6(4)	N(6)-Cu(1)-O(11A)	93.7(4)
N(1)-Cu(1)-O(31A′)	87.3(4)	N(3)-Cu(1)-O(31A′)	86.5(4)
N(4)-Cu(1)-O(31A′)	91.0(4)	N(6)-Cu(1)-O(31A′)	92.2(4)
O(11A)-Cu(1)-(31A′)	173.6(4)	N(11)-Cu(2)-N(9)	162.8(4)
N(11)-Cu(2)-N(7)	101.3(4)	N(9)-Cu(2)-N(7)	94.5(4)
N(11)-Cu(2)-N(8)	81.5(4)	N(9)-Cu(2)-N(8)	82.0(4)
N(7)-Cu(2)-N(8)	173.2(4)	N(7)-Cu(2)-O(12B)	91.1(4)
N(8)-Cu(2)-O(12B)	95.0(4)	N(9)-Cu(2)-(12B)	94.0(4)
N(11)-Cu(2)-O(12B)	92.6(4)	N(7)-Cu(2)-(33B′)	93.8(4)
N(8)-Cu(2)-O(33B′)	79.8(4)	N(9)-Cu(2)-(33B′)	79.4(4)
N(11)-Cu(2)-O(33B′)	92.6(4)	O(12B)-Cu(2)-(33B′)	172.0(4)

Symmetry code: A x, y, $z+1$; A′ x, $y-1$, $z+1$; B $x-0.5$, $0.5-y$, $0.5+z$; B′ x, $1-y$, $0.5+z$.

Table 3 Intermolecular hydrogen bonds

D—H···A	Symmetry code of A	Angles of DHA (°)	d (D···A) (nm)
N(2)—H(2)···O(14)	x, $y-1$, $z+1$	174.43	0.2951
N(3)—H(3)···O(11)	x, y, $z+1$	116.15	0.3144
H(5)—H(5)···O(22)	x, $-y$, $z+0.5$	148.98	0.3153
N(8)—H(8)···O(21)	$x-0.5$, $0.5-y$, $z-0.5$	154.58	0.3148
N(10)—H(10)···O(51)	x, y, z	151.72	0.2913

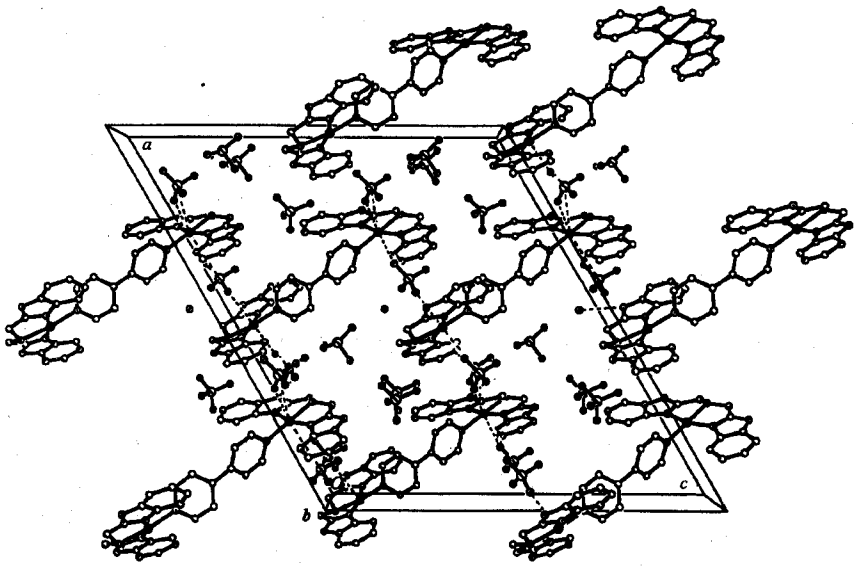

Fig. 2 Packing structure of the complex $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$.

Brief analysis for quantum chemistry calculation

According to molecular orbital theory, the frontier orbital and nearby molecular orbitals are the most important factors to the bioactivity.[11,12] The highest occupied molecular orbital (HOMO) and nearby occupied molecular orbitals are prior to donating electrons, but the lowest unoccupied molecular orbital (LUMO) and nearby unoccupied molecular orbitals are prior to accepting electrons. The components and high proportion (%) of frontier molecular orbitals are listed in Table 4. The components of 43 atoms of the computation model are larger in the LUMO and LUMO + 1. We can conclude that these atoms could accept electrons, this means that they could draw electron of $O_2^{-}\cdot$ effectively; meanwhile $O_2^{-}\cdot$ could move freely in the large space according to the analysis of the crystal structure, so the structural environment benefits $(O_2^{-}\cdot)_s$ to move close to and coordinate to the metal ions and the complex can have certain biological activity.

Table 4 Frontier molecular orbital components and proportion (%) of the complex ($C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$)

Atoms	HOMO − 1	HOMO	LUMO	LUMO + 1	Atoms	HOMO − 1	HOMO	LUMO	LUMO + 1
Cu(1)				1.02	C(19)				9.16
Cu(2)	23.19	40.19	0.20	0.45	C(20)				3.98
N(3)				0.16	C(21)				1.27
N(4)				2.46	C(22)		0.13		6.05
N(5)				1.70	C(23)	0.35	0.49		2.69
N(6)				5.93	C(24)	0.32	0.46		0.89
N(7)	4.47	8.89		4.21	C(25)	0.20	0.49		0.96
N(8)	5.74	8.93	0.19		C(26)	0.40	0.41		3.11
N(9)	11.44	11.64			C(27)	8.29	3.00		0.11
N(10)	1.21	1.24			C(28)				0.16
N(11)	2.70	4.74	1.38		C(29)	0.14			0.11
N(12)	0.16	0.25	0.81		C(30)	11.88	4.29		
C(1)				0.14	C(31)	6.84	3.17		
C(2)				0.37	C(32)	3.92			
C(3)				0.29	C(33)	8.20	3.54		
C(9)				0.16	C(34)	0.64	0.39	0.15	
C(10)				13.32	C(35)	0.17	0.32	0.11	
C(11)				1.36	C(36)	0.44	0.76	6.77	0.15
C(12)				11.45	C(37)	0.37	0.51	4.25	0.12
C(13)				4.27	C(38)			35.06	
C(14)				2.06	C(39)			0.21	0.16
C(15)				9.16	C(40)			26.72	0.35
C(16)				2.44	C(41)	0.10	0.13	2.67	1.21
C(17)				1.86	C(42)	0.20	0.25	13.60	1.25
C(18)				2.29					

Conclusions

According to the discussion in the text we can draw the conclusion as follows:

(1) The existance of large space in the crystal is the important micro-structural environment for $O_2^{-}\cdot$ moving freely.

(2) The weak coordinated groups are the important reason for this super molecular compound presenting biological activity.

(3) The contribution of forty-three atoms is lager in the LUMO and LUMO + 1 molecular orbits, they can accept the electron of $O_2^{-}\cdot$ or draw it together.

(4) The structure environment benefits $O_2^{-}\cdot$ to coordinate to metal ions and the complex can have certain biological activity.

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