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Magnetic Property and Crystal Structure of Alkoxo-bridged Bi- and Tetranuclear Copper(II) Complexes with Condensation Products of 3-Ethoxymethylene-2,4-pentanedione and Amino Alcohols

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Alkoxo-bridged polynuclear copper(II) complexes with condensation products of 3-ethoxymethylene-2,4-pentanedione and each of three amino alcohols, 2-aminoethanol, 3-amino-1-propanol, and 1-amino-2-propanol, were prepared and characterized by elemental analyses, infrared spectra, electronic spectra, molecular weight measurements, magnetic susceptibility measurements, and crystal structure analysis, the complexes being abbreviated as Cu(L-2), Cu(L-3), and Cu(L-2m), respectively. Cu(L-3) is a dimer, but Cu(L-2m) and Cu(L-2) are tetramers. The magnetic susceptibility of violet Cu(L-3), whose electronic spectrum exhibits a d-d band maximum at $17.7\times10^3\ \mathrm{cm}^{-1}$, is in conformity to the Bleaney-Bowers equation with exchange integral $-2J=920\ \mathrm{cm}^{-1}$. Cu(L-3) consists of alkoxo-bridged centrosymmetric binuclear units, where the geometries around the copper ion and bridged oxygen atom are planar and the angle of Cu–O–Cu is 103.6(1)°. The magnetisms of blue complexes Cu(L-2) and Cu(L-2m) exhibiting a d-d band maximum at $15.7\times10^3\ \mathrm{cm}^{-1}$ obey the Curie-Weiss law with positive Weiss constants 17 and 20 K, respectively, and are in accord with the Heisenberg model based on a tetranuclear cubane-like structure.

A great number of hydroxo- or alkoxo-bridged polynuclear copper(II) complexes have been studied in order to clarify the mechanism of magnetic interactions operating between copper(II) ions.[1–4] Hatfield *et al.*[1,2] found that the $2J$ value representing the copper(II)–copper(II) magnetic interaction correlates linearly with the angle of Cu–O–Cu, and emphasized the importance of the angle for the spin-exchange interaction. Kida and coworkers[3–9] investigated extensively the polynuclear copper(II) complexes with linear aliphatic amino alcohols such as $R_2N(CH_2)_nOH$, $R_2N(CH_2)_mX(CH_2)_nOH$, and $RS(CH_2)_mNH(CH_2)_nOH$ (R=alkyl; $m,n=2$ or 3; X=S, NH). Their conclusion with respect to the relationship between structure and magnetic property can be summarized as follows: (1) The planarity around the bridging oxygen atom is essentially important for the spin-exchange interaction rather than the angle of Cu–O–Cu; (2) the axial coordination accompanies deviation from the planarity around the oxygen atom and decreases the magnetic interaction; (3) the ring size of the chelate ring consisting of amino alcohol and copper ion is important in determining not only the planarity around the bridging oxygen atom, *i.e.*, the magnetic interaction, but also which the complex prefers to be, dimeric, trimeric, or tetrameric species. Two copper(II) complexes with each of ligands derived from 2,4-pentanedione and 2-aminoethanol or 3-amino-1-propanol (to be abbreviated as Cu(eia) and Cu(pia), respectively), may supply a set of typical examples for this point, since the complex Cu(pia) is a dimer with 0.41 BM. at room temperature, while the complex Cu(eia) is a cubane-like tetramer with 1.87 BM. at room temperature.[10]

In this study, polynuclear copper(II) complexes with Schiff base ligands derived from 3-ethoxymethylene-2,4-pentanedione and each of three amino alcohols, 2-aminoethanol, 3-amino-1-propanol, and 1-amino-2-propanol, have been prepared in order to examine their conclusion, (these complexes to be abbreviated as Cu(L-2), Cu(L-3), and Cu(L-2m), respectively). The complexes were characterized by elemental analyses, molecular weights, infrared spectra, electronic spectra, magnetic susceptibility measurements, and single-crystal X-ray analysis. Properties have been discussed in relation to the size of the chelate ring involving the amino alcohol and copper ion.

Experimental

Syntheses. 3-Ethoxymethylene-2,4-pentanedione was prepared from 2,4-pentanedione, acetic anhydride, and triethyl orthoformate according to the procedure of Riley and Busch.[11]

H_2L-2: To 50 cm³ of 98% ethanolic solution of 0.05 mol of freshly prepared 3-ethoxymethylene-2,4-pentanedione was slowly added 0.05 mol of 2-aminoethanol in 30 cm³ of ethanol at room temperature. After the reaction mixture had been allowed to stand for several hours in a refrigerator, white crystals which precipitated were collected and dried *in vacuo*. Found: C, 50.63; H, 8.02; N, 7.62%. Calcd for $C_8H_{13}NO_3\cdot H_2O$: C, 50.79; H, 7.93; N, 7.40%. IR: 3260 (ν_{OH}) and 1613 ($\nu_{C=N}$) cm^{-1}.

Cu(L-2): Ligand (H_2L-2), copper(II) acetate monohydrate, and sodium hydroxide in a mole ratio of 1:1:2 were mixed in ethanol and the mixture was refluxed for 1 h. The ethanol was removed by evaporation to dryness and dichloromethane was added. The resultant slurry was filtered and during the volume reduction of solution, crystalline Cu(L-2) was precipitated. It was recrystallized from a mixture of dichloromethane and methanol as dark blue crystals. Found: C, 40.97; H, 4.87; N, 6.01%. Calcd for $C_8H_{11}NO_3$-Cu: C, 41.28; H, 4.76; N, 6.01%.

Cu(L-2m) and Cu(L-3): Copper(II) complexes Cu(L-2m) and Cu(L-3) were prepared by mixing copper(II) acetate monohydrate, 3-ethoxymethylene-2,4-pentanedione, the corresponding amino alcohol, and sodium hydroxide in a mole ratio of 1:1:1:2 in ethanol. The mixture was refluxed for 1 h and the ethanol was removed to dryness by evaporation. The resultant solid was dissolved in dichloromethane and the solution was filtered, and during the volume reduction of solution, crystalline materials were precipitated. Complexes Cu(L-2m) and Cu(L-3) were recrystallized from a mixture of dichloromethane and methanol as dark blue rhombic and violet plate crystals, respectively. Found for Cu(L-2m): C, 43.39; H, 5.49; N, 5.25%. Calcd for $C_9H_{13}NO_3Cu$: C, 43.81; H, 5.31; N, 5.68%. Found for Cu(L-3): C, 43.68; H, 5.43; N, 5.69%. Calcd for $C_9H_{13}NO_3Cu$: C, 43.81; H, 5.31; N, 5.68%.

Physical Measurements. Infrared spectra were measured with Nujol mulls on a Shimadzu IR-410 spectrophotometer. Electronic spectra were recorded on a Hitachi 323 spectrophotometer in dichloromethane. Molecular weights were determined in benzene at 40 °C on a Corona vapor pressure osmometer Model 117. Magnetic susceptibilities were measured by the Faraday method in the temperature range from the liquid nitrogen temperature to room temperature. The apparatus was calibrated by use of $[Ni(en)_3]S_2O_3$.[12] The susceptibility was corrected for the diamagnetism of component atoms by use of Pascal's constants.[13] Effective magnetic moment was calculated from the equation $\mu_{\text{eff}}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the magnetic susceptibility per copper atom and $N\alpha$ is the temperature independent paramagnetism.

X-Ray Analysis of Cu(L-3). Violet plate-like crystals of Cu(L-3) were obtained by slow precipitation from a dichloromethane and methanol solution at room temperature. A crystal with approximate dimensions of $0.4\times0.5\times0.5$ mm³ was cut out from a large crystal and used for X-ray diffraction study. Unit-cell parameter and intensity data were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with a monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) at 24 ± 1 °C. Unit-cell parameters were determined by the least-squares refinement based on 20 reflections in the range $15°<2\theta<41°$. Crystal data: $C_{18}H_{26}N_2O_6Cu_2$, F.W.=493.5, monoclinic, space group=$P2_1/c$, $a=5.700(1)$, $b=8.654(3)$, $c=20.270(5)$ Å, $\beta=95.05(2)°$, $V=996.1(5)$ Å³, $D_x=1.645$ ($Z=2$), $D_m=1.61$ g cm^{-3} (by the flotation method in aqueous KI solution), μ(Mo $K\alpha$)$=13.4$ cm^{-1}.

Intensity data were collected by the θ-2θ scan technique with a scan rate of 8° min^{-1} in 2θ. For weak reflections the peak scan was repeated two or three times depending on their intensities. Three standard reflections were monitored every 100 reflections throughout the set to confirm no occurrence of decay in intensity. A total of 1756 reflections with $2.5°<2\theta<50°$ were collected, of which independent 1514 reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and used for structural analysis. Intensity data were corrected for the Lorentz and polarization effects but not for absorption because of the small crystal size and low absorption coefficient.

The structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares method. In the least-squares calculation, the function minimized was $\sum w(|F_o|-k|F_c|)^2$ where $w=1/\sigma(|F_o|)^2$. The neutral atomic scattering factors for H, C_{cov}, N, O, and Cu were taken from International Tables for X-Ray Crystallography, Vol. IV.[14] Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for all the component atoms were also taken from the literature.[14] All calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by use of the UNICS II Crystallographic Computing System.[15,16] The coordinates of the copper atom were easily obtained by an interpretation of Harker's peaks on the Patterson map. A Fourier synthesis based on the copper position revealed all the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters and then with anisotropic ones reduced the disagreement factors $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 6.00 and 7.55%, respectively. At this stage, a difference Fourier synthesis was calculated and located all the hydrogen atoms at chemically reasonable positions. Further refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms gave final values of 4.20 and 4.39% for R and R_w, respectively. The final difference Fourier synthesis showed no significant features.

TABLE 1. FINAL ATOMIC PARAMETERS FOR Cu(L-3)

A. Nonhydrogen atoms[a)]

Atom	x	y	z	B_{eq}/Å²
Cu	−285.2(10)	1392.1(6)	424.2(3)	2.4
O1	−1338(6)	−679(3)	303(2)	3.3
O2	1313(6)	3320(3)	463(2)	3.2
O3	1567(7)	6518(4)	1990(2)	5.0
N	−2189(6)	1937(4)	1116(2)	2.5
C1	−3072(9)	−1463(5)	628(2)	3.3
C2	−3361(9)	−757(6)	1302(2)	3.7
C3	−4097(9)	901(6)	1275(3)	3.8
C4	−1850(8)	3178(5)	1472(2)	2.6
C5	−186(8)	4371(5)	1417(2)	2.5
C6	1277(8)	4394(5)	893(2)	2.6
C7	2866(9)	5717(6)	765(3)	3.5
C8	−39(9)	5576(5)	1926(2)	3.2
C9	−1894(10)	5697(6)	2401(3)	3.9

B. Hydrogen atoms[a)]

Atom	x	y	z	B/Å²
H1A	−259(7)	−254(4)	70(2)	2.0(0.9)
H1B	−457(8)	−143(5)	35(2)	3.9(1.1)
H2A	−442(8)	−130(5)	151(2)	3.4(1.0)
H2B	−180(9)	−85(6)	161(2)	5.8(1.3)
H3A	−465(8)	123(5)	164(2)	3.6(1.1)
H3B	−524(8)	99(5)	93(2)	3.7(1.1)
H4	−290(7)	326(4)	181(2)	2.1(0.9)
H7A	210(7)	663(5)	77(2)	2.8(1.0)
H7B	423(8)	554(5)	101(2)	4.3(1.1)
H7C	338(7)	565(5)	38(2)	3.3(1.0)
H9A	−341(8)	575(5)	223(2)	3.5(1.0)
H9B	−167(9)	655(5)	268(2)	5.3(1.3)
H9C	−192(8)	489(5)	263(2)	4.2(1.1)

a) Atomic coordinates for nonhydrogen and hydrogen atoms have been multiplied by 10^4 and 10^3, respectively. The hydrogen atoms are labeled for identification by reference to the atoms to which they are attached.

Final positional parameters with estimated standard deviations are given in Table 1. Lists of structure factors (F_o and F_c) and anisotropic thermal parameters have been deposited as the supplementary data at the Chemical Society of Japan as Document No. 8312.

Results and Discussion

Infrared Spectra. The OH stretching vibration at 3260 cm^{-1} observed for the free ligand H_2L-2 is

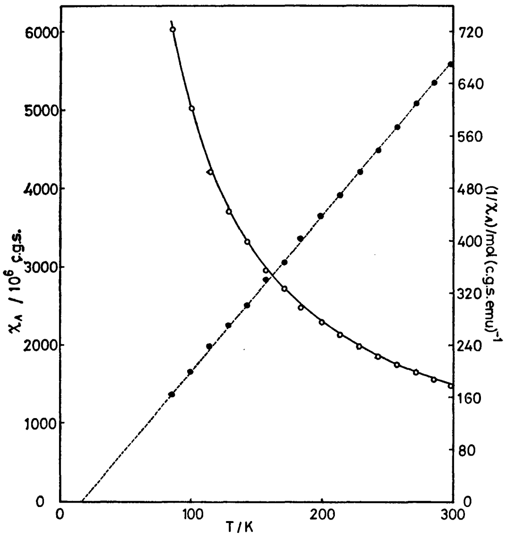

Fig. 1. Temperature dependence of magnetic susceptibility of Cu(L-2). Solid line of magnetic susceptibility represents the theoretical curve based on the equation (2) with the parameters of $J=40$ cm^{-1}, $J'=4$ cm^{-1}, $g=2.05$, $N\alpha=60\times10^{-6}$ c.g.s. emu/mol.

absent in complex Cu(L-2), indicating that alcoholic proton is lost upon the complexation.

Electronic Spectra. Visible and ultraviolet spectra of the complexes were obtained in dichloromethane and the band maxima are given in Table 2. Electronic spectra of the complexes consist of a broad band in the visible region assignable to the d-d transition with an extinction coefficient of the order of *ca.* 150 mol^{-1} dm^{-3} cm^{-1} and several bands in the ultraviolet region assignable to charge-transfer bands. The spectrum of complex Cu(L-3) exhibits a d-d transition band maximum at 17.7×10^3 cm^{-1}, while the spectra of complexes Cu(L-2) and Cu(L-2m) exhibit a band maximum at 15.5×10^3 cm^{-1}. This indicates that the coordination environment might be different between the two groups. The bands at *ca.* $(27-28)\times10^3$ cm^{-1} is characteristic of alkoxo-bridged copper(II) complexes and is assignable to the $p_\pi(O)\rightarrow d(Cu)$ charge-transfer transition.[3)]

Molecular Weights. Molecular weights were estimated by vapor pressure osmometry. The results were as follows: Found for Cu(L-3): 440; calcd for $C_{18}H_{26}N_2O_6Cu_2$ as dimer:496. Found for Cu(L-2): 920; calcd for $C_{32}H_{44}N_4O_{12}Cu_4$ as tetramer: 931. Found for Cu(L-2m): 925; calcd for $C_{36}H_{52}N_4O_{12}Cu_4$ as tetramer: 987. It is apparent that complexes Cu (L-2) and Cu(L-2m) with a five-membered chelate ring involving an amino alcohol and copper ion are tetramer, whereas complex Cu(L-3) with a six-membered chelate ring is dimer.

Magnetic Properties. The magnetic moment of complex Cu(L-3) is 0.35 BM. at room temperature, indicating the operation of a strong antiferromagnetic spin-exchange interaction between the copper(II) ions. The temperature dependence of the magnetic susceptibilities can be interpreted in terms of the following Bleaney-Bowers equation[17)] with a paramagnetic impurity term[18)] for the isotropic exchange interaction in a copper(II) dimer:

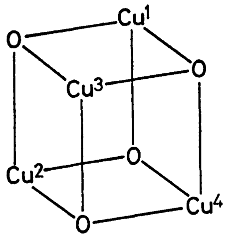

Fig. 2. Structure of tetranuclear cubane-like copper(II) complex.

TABLE 2. ELECTRONIC SPECTRAL DATA MEASURED IN DICHLOROMETHANE

Complex	Band maxima $\tilde{\nu}/10^3$ cm^{-1} (log ε)$^{a)}$			
Cu(L-3)	17.7(2.18)	27.7(3.85)	32.2(4.15)	37.3(4.45)
Cu(L-2)	15.7(2.16)	27.0(2.72)*	32.4(4.14)*	36.7(4.45)
Cn(L-m)	15.7(2.21)	27.3(2.72)	32.8(3.96)*	36.4(4.06)*

a) Symbol * means shoulder.

$$\chi_A=\frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp(-2J/kT)\right]^{-1}(1-p)+\frac{0.45p}{T}+N\alpha, \tag{1}$$

where χ_A is the magnetic susceptibility per copper ion, p is the ratio of mononuclear copper(II) ions to total copper(II) ions, and N, g, J, β, and $N\alpha$ have the usual meanings. The experimental data fit Eq. 1 with magnetic parameters $-2J=920$ cm^{-1}, $g=2.10$, $p=0.01$, and $N\alpha=60\times10^{-6}$ c.g.s. emu/mol.

The magnetic moments of complexes Cu(L-2) and Cu(L-2m) are 1.88 and 1.86 BM. at room temperature, respectively. As shown in Fig. 1, the magnetisms of complexes Cu(L-2) and Cu(L-2m) obey the Curie-Weiss law with positive Weiss constants 17 and 20 K, respectively, indicating that a ferromagnetic interaction is operative in these complexes. For complexes with this kind of magnetic properties, the tetranuclear cubane-like structure shown in Fig. 2 has been assumed and the temperature dependence of their magnetic properties has been interpreted on the basis of the Heisenberg model.[6,15)] The Hamiltonian for the spin-exchange interaction of a tetranuclear structure may be written as $H=-2J_{12}S_1S_2-2J_{13}S_1S_3-2J_{14}S_1S_4-2J_{23}S_2S_3-2J_{24}S_2S_4-2J_{34}S_3S_4$, where the numbering of copper ions are given in Fig. 2. On assuming $J=J_{13}=J_{24}$ and $J'=J_{12}=J_{23}=J_{34}=J_{14}$, magnetic susceptibilities are given by

$$\begin{aligned}\chi_A = {} & 3g^2\{10\exp[(J+2J')/kT]+4\exp(-J/kT)\\ & +2\exp[(J-2J')/kT\}/32T\{4\exp[(J+2J')/kT]\\ & +5\exp(-J/kT)+\exp(-Q(11)/kT)\\ & +\exp(-Q(22)/kT)+\exp(-Q(33)/kT)\\ & +\exp(-Q(44)/kT)+3\exp[(J-2J')/kT]\}+N\alpha, \end{aligned} \tag{2}$$

where $Q(11)$, $Q(22)$, $Q(33)$, and $Q(44)$ have the same meanings as those used by Hatfield and Inman.[19)] The exchange integral (J, J'), g, and $N\alpha$ were evaluated from the best-fit of experimental data to Eq. 2. The evaluated values for Cu(L-2) are $J=40$ cm^{-1},

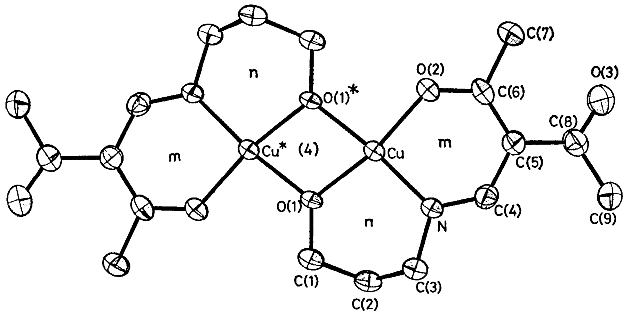

Fig. 3. Molecular structure of Cu(L-3) with the atom numbering scheme.

$J'=4\ \mathrm{cm}^{-1}$, $g=2.05$, and $N\alpha=60\times10^{-6}$ c.g.s. emu/mol, and those for Cu(L-2m) are $J=40\ \mathrm{cm}^{-1}$, $J'=5\ \mathrm{cm}^{-1}$, $g=2.10$, and $N\alpha=60\times10^{-6}$ c.g.s. emu/mol. It is found that the magnetic behavior of complexes Cu(L-2) and Cu(L-2m) can be interpreted in terms of Eq. 2 formulated on the basis of the tetranuclear cubane-like structure and the assumption that both J and J' are positive.

Molecular Structure of Cu(L-3). The molecular structure of complex Cu(L-3) consists of discrete alkoxo-bridged centrosymmetric binuclear units, as deduced on the molecular weight measurement and magnetic behavior. An ORTEP plot of the perspective molecule is shown in Fig. 3, with the atom numbering scheme. Bond lengths and angles with estimated standard deviations are given in Table 3.

The coordination geometry around the copper ion is a square planar within ±0.01 Å for deviations of the component atoms. The geometries of $\mathrm{Cu}\begin{matrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{matrix}\mathrm{Cu}$ and around the bridging oxygen atom are perfectly planar. Such a structural feature is similar with the related copper(II) complex Cu(pia) containing the ligand derived from 2,4-pentanedione and 3-amino-1-propanol,[10] and has been observed for binuclear copper(II) complexes associated with strong antiferromagnetic interaction.[4] The Cu–O–Cu angle 103.6(1)° is smaller than that of Cu(pia) (106°).[10] The saturated six-membered chelate ring containing amino alcohol has a chair conformation, and atoms Cu and C(2) are displaced by −0.13 and 0.70 Å, respectively, from the plane through O(1), C(1), C(3), and N. The acetyl group is tilted to the unsaturated six-membered chelate ring by 12.5° due to the steric hindrance between the acetyl and methyl groups attached to the unsaturated chelate ring. This steric hindrance is also found in the deviations of O(3) and C(7) by 0.21 and −0.16 Å, respectively, from the plane through atoms C(5), C(6), and C(8).

Based on the above-described results, it has been established that complexes Cu(L-2) and Cu(L-2m) with a five-membered chelate ring consisting of amino alcohol and copper ion are of tetranuclear cubane-like structure associated with ferromagnetic interaction, whereas complex Cu(L-3) with a six-membered chelete ring is a dimer associated with strong antiferromagnetic interaction. Mikuriya *et al.*[20] examined a number of molecular structures of alkoxo-bridged polynuclear copper(II) complexes and pointed out that for the formation of binuclear copper(II) complexes the favorable chelate ring system is the 6-6-(4)-6-6 and 5-6-(4)-6-5 fused chelate ring systems, and that the 6-5-(4)-5-6 system often forms a stable tetranuclear species, where the fused chelate ring system is represented by m-n-(4)-n-m according to their notation (Fig. 3). The complexes prepared in this study supply good examples to support their suggestions. The planarity around the bridging oxygen atom should be mainly attributable to the conformation of the chelate ring involving amino alcohol and copper ion. It can be considered that in the case of complex Cu(L-3) the chair conformation of the six-membered chelate ring allows a planar geometry around the bridging oxygen atom and that the complex prefers to be a dimer associated with strong antiferromagnetic interaction. On the other hand, for complexes Cu(L-2) and Cu(L-2m) with a five-membered chelate ring, it can be considered that the deviation from the planar geometry around the bridging oxygen atom should occur and that the oxygen atom can coordinate to another copper ion to form a tetranuclear copper(II) complex, since a five-membered chelate ring takes a gauche or envelope conformation.

TABLE 3. BOND DISTANCES AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, FOR Cu(L-3)[a)]

Bond distance	l/Å		l/Å
Cu···Cu*	2.994(1)	N-C (4)	1.299(5)
Cu-O (1)	1.899(3)	C (4)-C (5)	1.412(6)
Cu-O (1)*	1.910(3)	C (5)-C (6)	1.407(6)
Cu-N	1.905(3)	C (5)-C (8)	1.463(6)
Cu-O (2)	1.899(3)	O (2)-C (6)	1.275(5)
O (1)-C (1)	1.408(6)	C (6)-C (7)	1.496(6)
C (1)-C (2)	1.517(6)	C (8)-O (3)	1.224(6)
C (2)-C (3)	1.494(7)	C (8)-C (9)	1.494(7)
N-C (3)	1.467(6)		
Bond angle	ϕ/°		ϕ/°
Cu-O(1)-Cu*	103.6(1)	Cu-N-C(4)	123.1(3)
Cu-O(1)-C(1)	128.3(2)	C(3)-N-C(4)	117.3(3)
Cu*-O(1)-C(1)	127.7(2)	N-C(4)-C(5)	128.9(4)
O(1)-Cu-O(1)*	76.3(1)	C(4)-C(5)-C(6)	121.0(3)
O(1)-Cu-N	97.7(1)	C(4)-C(5)-C(8)	117.5(4)
N-Cu-O(2)	93.0(1)	C(6)-C(5)-C(8)	121.3(4)
O(1)*-Cu-O(2)	93.0(1)	C(5)-C(6)-O(2)	123.4(4)
O(1)-Cu-O(2)	168.3(1)	C(5)-C(6)-C(7)	123.3(3)
O(1)*-Cu-N	173.2(1)	O(2)-C(6)-C(7)	113.1(4)
O(1)-C(1)-C(2)	111.2(3)	Cu-O(2)-C(6)	129.2(3)
C(1)-C(2)-C(3)	113.9(4)	C(5)-C(8)-O(3)	123.1(4)
C(2)-C(3)-N	112.5(4)	C(5)-C(8)-C(9)	120.1(4)
Cu-N-C(3)	119.4(2)	O(3)-C(8)-C(9)	116.7(4)

a) Symbol * means $-x$, $-y$, $-z$.

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