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Binuclear Metal Complexes. LII [1]. Synthesis, Spectral and Magnetic Properties of Binuclear Copper(II) Complexes of Amides Derived from 3-Amino-1-propanol and Various Amino Acids, and Crystal Structure of Copper(II) Complex of α-Amino-isobutyric Acid Derivative

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Binuclear copper(II) complexes with amides derived from 3-amino-1-propanol and various amino acids were prepared and characterized by elemental analysis, infrared and electronic spectra and magnetic susceptibilities (78–300 K). They exhibit a band around 28×10^3 cm^{-1} characteristic of alkoxo-bridged structure and show a very strong antiferromagnetic interaction. The crystal structure of one of them, $[Cu_2\{NH_2C(CH_3)_2CONCH_2CH_2CH_2O\}_2]$, was determined by the single-crystal X-ray diffraction method. Crystals are monoclinic, space group $P2_1/n$, $a = 16.661(6)$, $b = 10.256(4)$, $c = 5.333(1)$ Å; $\beta = 98.69(2)°$. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an R factor of 0.038. The crystal structure consists of alkoxo-bridged binuclear units. The coordination geometry about the copper ion is square-planar. The structure detail is in harmony with the magnetic and spectral properties.

Introduction

Copper(II) complexes of amino acids or their derivatives have been studied extensively because of their possibility as simple models for the binding of metal ions to proteins. However, most of the work in this area has dealt with mononuclear complexes. Binuclear copper(II) complexes with amino acid derivatives so far reported are complexes of Schiff bases derived from amino acids and salicylaldehyde [2] or 3-formyl-5-methylsalicylaldehyde [3], and of some amide derivatives of amino acids such as N-acetylglycine, N-benzoylglycine and N-acetyl-L-alanine [4]. These complexes showed a relatively strong antiferromagnetic spin-exchange interaction ($-2J = 115$–447 cm^{-1}). Such binuclear copper(II) complexes are currently under extensive study as model systems of type 3 copper. Magnetic susceptibility studies on type 3 copper proteins have established that a strong antiferromagnetic coupling ($-2J \geqslant 500$ cm^{-1}) is present between the two copper atoms [5]. In mimicing the properties of type 3 copper it is important to examine the model systems containing amino acids that bring about a strong antiferromagnetic interaction.

Binuclear copper(II) complexes of amides derived from 3-amino-1-propanol and glycine or alanine were prepared by Ojima and Yamada [6]. Interestingly, these complexes have extremely low magnetic moments (0.42–0.66 B.M.) at room temperature, suggesting the presence of a very strong antiferromagnetic interaction between the copper ions. However, cryomagnetic investigations of these complexes have not yet been reported. In order to characterize this type of complex more fully, we decided to extend Ojima and Yamada's complexes to other amino acids and to see whether the complexes formed showed different properties according to a wide variety of amino acids. Thus, in this study we have prepared new binuclear copper(II) complexes of amides derived from 3-amino-1-propanol and various amino acids (Fig. 1, abbreviated as Cu_2(aa-nno)$_2$) and measured the temperature dependence of their magnetic susceptibilities (78–300 K) and their electronic spectra. Moreover, we carried out a single-crystal X-ray structure analysis of Cu_2(aiba-nno)$_2$ (where H_2aiba-nno denotes the amide derived from 3-amino-1-propanol and α-aminoisobutyric acid) in order to discuss the magnetic and spectral properties in terms of the molecular structure.

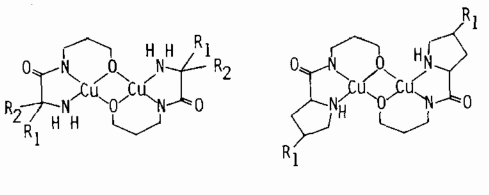


Fig. 1. The Cu_2(aa-nno)$_2$ complexes.

Experimental

Preparation of the Complexes

The ligands were prepared from 3-amino-1-propanol and amino acids by the method of Ojima and Yamada [6]. Amino acids used in this study are glycine, L-alanine, α-aminobutyric acid, norvaline, norleucine, L-leucine, L-isoleucine, α-aminoisobutyric acid, L-methionine, L-phenylalanine, L-proline, and L-hydroxyproline. The complexes were prepared by the following method. Equimolar of the ligand and copper(II) hydroxide were mixed in water. The mixture was heated on a steam bath for 1 h, filtered while hot, and allowed to stand for several days. Red-purple needles separated and were collected and dried in a P_2O_5 desiccator under reduced pressure. The complexes were recrystallized from water or methanol. The results of elemental analyses are listed in Table I with their abbreviations.

Measurements

Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Copper analysis was carried out with a Shimadzu Atomic Absorption-Flame Spectrophotometer Model AA-610. Water and methanol in crystal were analysed thermogravimetrically with a Rigaku Thermoanalyser.

Infrared spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 in the region 4000–650 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 at room temperature. Magnetic susceptibility was measured by the Faraday method from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$. The susceptibility was corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants. Effective magnetic moment was calculated from the equation, $\mu_{eff} = 2.828\sqrt{(\chi_A - N\alpha)T}$, where χ_A is the atomic magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism [7].

X-Ray Crystal Structure Analysis of Cu$_2$(aiba-nno)$_2$

A crystal with dimensions of 0.20 × 0.32 × 0.32 mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 19 ± 1 °C. The unit-cell parameters were determined by the least-squares refinement based on the 25 reflections in the range of $24 < 2\theta < 34°$.

Crystal Data: $C_{14}H_{28}N_4O_4Cu_2$, F.W. = 443.49; monoclinic; $P2_1/n$; a = 16.661(6), b = 10.256(4), and

TABLE I. Abbreviations and Analytical Data of Complexes.

Complex abbrev.	R_1 R_2	Found (Calcd) (%)				
		C	H	N	Cu	Solv.
Cu_2(gly-nno)$_2$	H H	30.95(31.01)	5.20(5.20)	14.35(14.46)	32.5(32.8)	
Cu_2(ala-nno)$_2$	H CH_3	34.67(34.69)	5.91(5.82)	13.33(13.49)	30.7(30.6)	
Cu_2(anba-nno)$_2$	H CH_2CH_3	37.84(37.92)	6.43(6.36)	12.68(12.63)	27.9(28.7)	
Cu_2(nva-nno)$_2$·2CH_3OH	H $CH_2CH_2CH_3$	40.08(40.36)	7.54(7.53)	10.57(10.46)	23.3(23.7)	11.97(11.96)
Cu_2(nle-nno)$_2$·1/2H_2O	H $CH_2CH_2CH_2CH_3$	42.59(42.51)	7.32(7.33)	11.16(11.02)	24.9(25.0)	1.91(1.77)
Cu_2(leu-nno)$_2$·H_2O	H $CH_2CH(CH_3)_2$	42.00(41.77)	7.47(7.40)	10.79(10.82)	24.6(24.6)	3.61(3.48)
Cu_2(ile-nno)$_2$	H $CH(CH_3)CH_2CH_3$	42.86(43.27)	7.57(7.26)	10.82(11.21)	25.5(25.4)	
Cu_2(aiba-nno)$_2$	CH_3 CH_3	37.86(37.92)	6.36(6.36)	12.61(12.63)	28.0(28.7)	
Cu_2(met-nno)$_2$	H $CH_2CH_2SCH_3$	35.60(35.88)	6.56(6.02)	10.37(10.46)	23.2(23.7)	
Cu_2(phe-nno)$_2$·CH_3OH	H $CH_2C_6H_5$	49.20(50.07)	5.98(6.05)	9.28(9.34)	20.6(21.2)	5.24(5.34)
Cu_2(pro-nno)$_2$	H –	41.01(41.11)	6.06(6.04)	11.84(11.98)	27.9(27.2)	
Cu_2(hyp-nno)$_2$·3/2H_2O	OH –	36.51(36.50)	6.03(5.93)	10.71(10.64)	23.3(24.1)	

$c = 5.333(1)$ Å; $\beta = 98.69(2)^\circ$; $D_m = 1.63$ (by floatation in $CCl_4-CH_2BrCH_2Br$); $D_c = 1.64$ g cm^{-3}; $Z = 2$; μ(Mo Kα) = 23.9 cm^{-1}.

The intensity data were collected by the $2\theta-\omega$ scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to four times depending on the intensities. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 1952 reflections with $2\theta < 52^\circ$ were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 1597 reflections with $|F_o| \geqslant 3\sigma(F_o)$ were considered as 'observed' and were used for the structure analysis.

The structure was solved by the heavy-atom method. Refinement was carried out by the block-diagonal least-squares method. All the hydrogen atoms were located from the subsequent difference Fourier map. The final R values were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.038$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.056$. The weighting scheme was $w = (4.6 + |F_o| + 0.013|F_o|^2)^{-1}$ [7]. The final difference Fourier synthesis showed no peaks higher than 0.52 e/Å^3.

All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version [8] of the UNICS-III [9] and the ORTEP [10] programs. Lists of the structure factors and anisotropic thermal parameters are available from the Editor. The final positional and thermal parameters with their estimated standard deviations are given in Table II.

TABLE II. Fractional Positional Parameters (×10^4 for Non-Hydrogen Atoms; ×10^3 for Hydrogen Atoms) and Thermal Parameters with Their Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B_{eq} or B/Å^2
Cu	849.9(2)	4597.6(4)	6060(1)	2.02
O(1)	−267(1)	4232(3)	6311(5)	2.92
O(2)	2521(1)	2694(3)	10821(5)	2.97
N(1)	1321(2)	3398(3)	8590(5)	2.19
N(2)	1998(2)	4896(3)	5531(5)	2.27
C(1)	−528(2)	3346(4)	8063(7)	2.89
C(2)	40(2)	2187(4)	8518(8)	3.09
C(3)	865(2)	2515(4)	10001(7)	2.78
C(4)	2116(2)	3398(3)	9186(6)	1.87
C(5)	2569(2)	4400(3)	7762(6)	1.82
C(6)	2811(3)	5524(3)	9585(7)	2.85
C(7)	3316(2)	3795(4)	6894(8)	2.96
H1(C(1))	−113(3)	299(4)	734(8)	3.9(10)
H2(C(1))	−54(3)	383(4)	987(9)	3.5(9)
H1(C(2))	14(3)	179(4)	670(8)	3.3(9)
H2(C(2))	−23(3)	144(4)	959(9)	3.6(9)
H1(C(3))	121(3)	162(4)	1041(8)	2.9(8)
H2(C(3))	79(3)	298(5)	1178(9)	4.6(11)
H1(C(6))	314(3)	625(4)	869(8)	3.1(9)
H2(C(6))	320(3)	516(5)	1125(9)	4.1(10)
H3(C(6))	228(3)	595(5)	1015(8)	3.6(9)
H1(C(7))	363(3)	452(4)	592(9)	3.6(10)
H2(C(7))	314(3)	299(4)	562(8)	3.1(9)
H3(C(7))	373(3)	344(4)	852(9)	3.6(9)
H1(N(2))	210(3)	593(5)	531(8)	3.5(9)
H2(N(2))	211(3)	440(4)	385(10)	4.1(11)

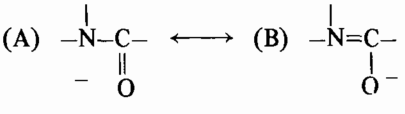
Results and Discussion

Description of the Structure of Cu$_2$(aiba-nno)$_2$

A perspective drawing of the molecule and the numbering system are illustrated in Fig. 2. Bond lengths and angles are listed in Table III.

The crystal structure consists essentially of alkoxo-bridged binuclear unit which has a center of symmetry. The Cu–Cu^i distance is 3.002(1) Å and the Cu–O–Cu^i angle is 103.5(1)°. The coordination geometry around the copper ion is square-planar. The square plane around the copper atom is formed by two alkoxo oxygen, a deprotonated amide nitrogen and an amino nitrogen atoms. As seen in Table IV, four coordinating atoms around the copper atom are almost coplanar with the deviations within ±0.06 Å. The Cu–O bond lengths (1.923(3) and 1.900(3) Å) and the Cu–N(amine) bond length (1.999(3) Å) fall in the range of those of the other alkoxo-bridged binuclear copper(II) complexes [7, 11]. The Cu–N(amide) distance (1.905(3) Å) is significantly shorter than the Cu–N(amine) distance and is comparable with other deprotonated amide and peptide complexes [12].

The N(1)–C(4) bond length (1.315(4) Å) is shorter than the normal N–C single bond distance and the O(2)–C(4) bond (1.248(4) Å) is slightly longer than the C=O double bond distance [13]. This implies a contribution of the resonance form B [12]:



$$(A)\ -\overset{\overset{Cu}{|}}{N}-\underset{\underset{O}{\|}}{C}-\ \overset{-}{} \longleftrightarrow (B)\ -\overset{\overset{Cu}{|}}{N}=\underset{\underset{O^-}{|}}{C}-$$

The $C(3)-N(1)-\overset{\overset{C(5)}{|}}{C}(4)=O(2)$ moiety is almost planar because of the presence of the deprotonated peptide group. The bonds attached to the amide nitrogen atom and those to the bridging oxygen atom are both coplanar (sums of the bond angles subtended at N(1) and O(1) are 360.0° and 359.9°, respectively). Therefore, in the six-membered ring, $\overline{Cu-O(1)-C(1)-C(2)-C(3)-N(1)}$, Cu, O(1), C(1), C(3), and N(1) are nearly in a plane, while C(2) deviates from

TABLE III. Interatomic Distances (Å) and Bond Angles (°) with Their Estimated Standard Deviations in Parentheses.

(a) Copper coordination spheres			
Cu–Cu^{i}*	3.002(1)	Cu–N(1)	1.905(3)
Cu–O(1)	1.923(3)	Cu–N(2)	1.999(3)
Cu–O(1)^{i}	1.900(3)		
Cu–O(1)–Cu^{i}	103.5(1)	O(1)^{i}–Cu–N(1)	173.4(1)
O(1)–Cu–O(1)^{i}	76.5(1)	O(1)^{i}–Cu–N(2)	102.3(1)
O(1)–Cu–N(1)	97.1(1)	N(1)–Cu–N(2)	84.2(1)
O(1)–Cu–N(2)	175.3(1)		
(b) Ligand moiety			
O(1)–C(1)	1.419(5)	O(2)–C(4)	1.248(4)
C(1)–C(2)	1.515(5)	C(4)–C(5)	1.542(5)
C(2)–C(3)	1.517(5)	N(2)–C(5)	1.496(4)
N(1)–C(3)	1.461(5)	C(5)–C(6)	1.523(5)
N(1)–C(4)	1.315(4)	C(5)–C(7)	1.524(5)
Cu–O(1)–C(1)	124.6(2)	N(1)–C(4)–C(5)	115.6(3)
Cu^{i}–O(1)–C(1)	131.8(2)	O(2)–C(4)–C(5)	118.4(3)
O(1)–C(1)–C(2)	111.2(3)	N(2)–C(5)–C(4)	108.6(2)
C(1)–C(2)–C(3)	113.9(3)	C(4)–C(5)–C(6)	107.0(3)
N(1)–C(3)–C(2)	111.7(3)	C(4)–C(5)–C(7)	111.2(3)
C(3)–N(1)–C(4)	117.3(3)	N(2)–C(5)–C(6)	109.0(3)
Cu–N(1)–C(3)	125.1(2)	N(2)–C(5)–C(7)	110.3(3)
Cu–N(1)–C(4)	117.6(2)	C(6)–C(5)–C(7)	110.6(3)
N(1)–C(4)–O(2)	126.0(3)	Cu–N(2)–C(5)	110.0(2)

*Superscript (i) refers to the equivalent position (–x, 1 – y, 1 – z).

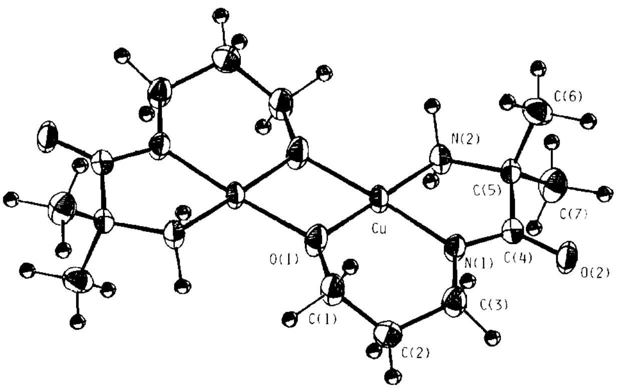


Fig. 2. Molecular structure of $Cu_2(aiba\text{-}nno)_2$. Thermal ellipsoids are drawn at the 50% probability level.

TABLE IV. Deviations of the Atoms from Least-squares Planes (Å).

(I) Plane through O(1), N(1), N(2), O(1)^{i}
$-0.0499X + 0.7147Y + 0.6972Z = 5.5253^{a}$
[O(1) –0.054, N(1) 0.049, N(2) –0.047, O(1)^{i} 0.052, Cu 0.027, O(2) 0.263, C(1) –0.031, C(2) –0.758, C(3) –0.035, C(4) 0.205, C(5) 0.372, C(6) 1.854, C(7) –0.457]^{b}

(II) Plane through O(1), C(1), C(3), N(1)
$-0.0780X + 0.7072Y + 0.7064Z = 5.5059$
[O(1) –0.024, C(1) 0.027, C(3) –0.026, N(1) 0.023, Cu 0.001, C(2) –0.716]

(III) Plane through Cu, N(1), N(2)
$-0.0172X + 0.7312Y + 0.6767Z = 5.6104$
[Cu 0.000, N(1) 0.000, N(2) 0.000, C(4) 0.192, C(5) 0.417]

(IV) Plane through N(1), C(4), C(5), O(2)
$-0.1844X + 0.6843Y + 0.7253Z = 5.2977$
[N(1) 0.004, C(4) –0.010, C(5) 0.003, O(2) 0.004, Cu 0.012, C(3) 0.070, N(2) –0.336]

[a] The equation of the plane is expressed as LX + MY + NZ = D, where X, Y, and Z in Å units refer to the crystallographic axes. [b] Deviations (Å) of atoms from the planes are listed in square brackets. Superscript (i) refers to the equivalent position (–x, 1 – y, 1 – z).

the plane by 0.716 Å. The five-membered chelate ring, Cu–N(1)–C(4)–C(5)–N(2), assumes an envelope conformation, *i.e.*, both carbon atoms, C(4) and C(5), are placed in the same side of the Cu–N(1)–N(2) plane (Table IV).

The carboxyl oxygen atom, O(2), participates in hydrogen bonding with the terminal amino nitrogen atom, N(2), of the neighboring complex (O(2)---N(2) (1/2 – x, –1/2 + y, 3/2 – z) 3.094(4) Å).

Infrared Spectra

Infrared spectra of the free ligands show a strong band around 3350 cm^{-1}, which is attributed to the OH stretching vibration. This band is absent in the spectra of the complexes [7]. In the complexes the amide I (at ~1640 cm^{-1}) and amide II (at ~1550 cm^{-1}) bands [14] of the free ligands are replaced by a strong absorption at ~1560 cm^{-1} which may be assigned to a C=O stretching mode. These facts suggest that both the alcoholic and amide protons are lost upon complexation. From the analytical and the IR data we concluded that the present complexes consist of neutral binuclear molecules with the general formula $Cu_2(aa\text{-}nno)_2$. This has been confirmed by the X-ray structure analysis in the case of $Cu_2(aiba\text{-}nno)_2$.

Magnetic Properties

Magnetic moments per copper atom are very low at room temperature, indicating that a strong antiferromagnetic interaction is operating between the copper(II) ions. The magnetic susceptibilities were measured over the temperature range 78–300 K. The temperature dependences of magnetic susceptibilities for $Cu_2(ile\text{-}nno)_2$ and $Cu_2(aiba\text{-}nno)_2$ are shown in Fig. 3 as examples. The magnetic behaviors of the present complexes can be interpreted by the modified Bleaney–Bowers equation [7]

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

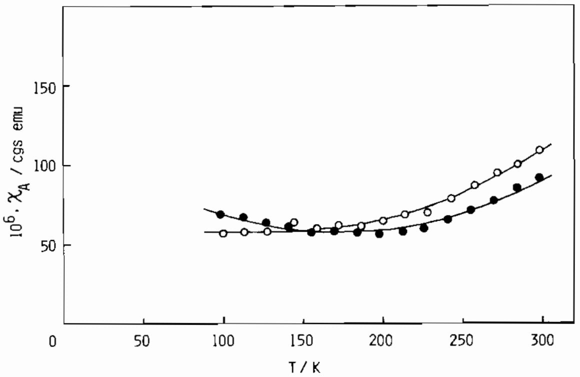


Fig. 3. Temperature dependence of magnetic susceptibilities of Cu_2(ile-nno)$_2$ (○) and Cu_2(aiba-nno)$_2$ (●). The solid curves were calculated from eqn. 1 using the parameters listed in Table V.

where χ_A is the susceptibility per copper atom, P is the mole fraction of the mononuclear copper(II) impurity, and other symbols have the usual meanings. The second term in eqn. 1 was added to account for the presence of the small amount of a paramagnetic impurity which was found in some samples. The parameters, $-2J$, g, $N\alpha$, and P were evaluated from the best fit of the experimental data to eqn. 1 and are listed in Table V. The $-2J$ values, the energy separation between the spin-singlet ground state and the lowest spin-triplet state, were evaluated at 805–1080 cm^{-1}. In the case of the related binuclear copper(II) complexes with the diaminoalcohols, $Cu_2\{R_2N(CH_2)_mNH(CH_2)_nO\}_2X_2$ (where $R = H$, CH_3, and C_2H_5, $m = 2$ and 3, $n = 2$ and 3; $X = ClO_4$ and $B(C_6H_5)_4$), $-2J$ values are 495–700 cm^{-1} [15]. Therefore, the antiferromagnetic interaction seems to become stronger when the deprotonated amide nitrogen is substituted for the amino nitrogen. In $Cu_2\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}_2(CH_3OH)_2(ClO_4)_2$ and $Cu_2\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_3O\}_2(H_2O)(ClO_4)_2$, the coordination geometry around the copper ion is five-coordinated square pyramid and the apical site is occupied by CH_3OH, H_2O or ClO_4^- with Cu–O distance of 2.34–2.62 Å [11]. The axial coordination should have the effect on the copper atom of lifting its position from the basal plane toward the axial ligand (by 0.19–0.25 Å) and may be a factor in depressing the antiferromagnetic interaction. On the other hand, in the case of the present complexes there are no anions to coordinate at the axial position. In addition to this, no formal charge was left on the copper atoms so that further coordination is not feasible. In fact, there is no axial coordination in Cu_2(aiba-nno)$_2$ and the coordination is nearly perfectly coplanar. These structural features brought about such a strong antiferromagnetic interaction between the copper(II) ions [16, 17].

Electronic Spectra

The band maxima of the electronic absorption spectra in nujol mull and in water are given in Table VI. The spectra are in general contour similar to those of the binuclear copper(II) complexes with the corresponding diaminoalcohols, $Cu_2\{R_2N(CH_2)_mNH(CH_2)_nO\}_2X_2$ [15], but the d–d bands for the present complexes (18.1×10^3 cm^{-1}) are higher in frequency compared with those ($15–17 \times 10^3$ cm^{-1}) of the binuclear copper(II) complexes with the diaminoalcohols. The blue-shift of the d–d bands may be attributed to the square planar arrangement of the complexes. The more intense band at 28.5×10^3 cm^{-1} is characteristic of alkoxo-bridged structure [6] and may be assigned to the $p_\pi(O) \rightarrow d_\sigma(Cu)$ transition [7, 15]. The frequencies of the CT bands are slightly higher than those ($25–28 \times 10^3$ cm^{-1}) for the binuclear copper(II) complexes with the diaminoalcohols. Since the energy of the d_σ orbital is much more strongly affected by the coordination manner than that of the $p_\pi(O)$ orbital, the high values of $\tilde{\nu}_{max}$ may be interpreted in terms of the raising of the d_σ orbital in energy due to the planar coordination in the present complexes [18].

TABLE V. Magnetic Data of Cu_2(aa-nno)$_2$.

Complex	μ_{eff}/BM	(K)	$2J/cm^{-1}$	g	$N\alpha \times 10^6$/cgs emu	P
Cu_2(gly-nno)$_2$	0.35	(294)	960	2.10	17	0
Cu_2(ala-nno)$_2$	0.33	(293)	1000	2.10	21	0
Cu_2(anba-nno)$_2$	0.48	(298)	965	2.10	100	0.029
Cu_2(nva-nno)$_2 \cdot 2CH_3OH$	0.33	(297)	1080	2.20	58	0
Cu_2(nle-nno)$_2 \cdot 1/2H_2O$	0.29	(291)	1025	2.10	61	0
Cu_2(leu-nno)$_2 \cdot H_2O$	0.55	(293)	805	2.10	70	0.020
Cu_2(ile-nno)$_2$	0.35	(298)	970	2.10	58	0
Cu_2(aiba-nno)$_2$	0.36	(297)	1015	2.10	38	0.007
Cu_2(met-nno)$_2$	0.46	(298)	900	2.05	40	0.018
Cu_2(phe-nno)$_2 \cdot CH_3OH$	0.34	(296)	970	2.10	60	0
Cu_2(pro-nno)$_2$	0.40	(294)	865	2.05	57	0
Cu_2(hyp-nno)$_2 \cdot 3/2H_2O$	0.48	(289)	855	2.10	42	0.013

TABLE VI. Spectral Data of $Cu_2(aa\text{-}nno)_2$.

Complex	Mull spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}		Solution spectra $\tilde{\nu}_{max}/10^3$ cm^{-1} (ϵ)	
$Cu_2(gly\text{-}nno)_2$	18.9	28.0	17.9(65)	28.7(1110)
$Cu_2(ala\text{-}nno)_2$	19.1	27.5	18.1(67)	28.6(1100)
$Cu_2(anba\text{-}nno)_2$	18.9	27.0	18.2(68)	28.6(1250)
$Cu_2(nva\text{-}nno)_2 \cdot 2CH_3OH$	19.3	27.4	18.2(67)	28.5(1090)
$Cu_2(nle\text{-}nno)_2 \cdot 1/2H_2O$	19.1	27.0	18.2(80)	28.5(1550)
$Cu_2(leu\text{-}nno)_2 \cdot H_2O$	18.9	27.2	18.1(68)	28.5(1290)
$Cu_2(ile\text{-}nno)_2$	18.9	27.4	18.1(65)	28.4(1160)
$Cu_2(aiba\text{-}nno)_2$	19.1	27.4	18.1(70)	28.4(1240)
$Cu_2(met\text{-}nno)_2$	19.1	28.0	18.1(68)	28.5(1250)
$Cu_2(phe\text{-}nno)_2 \cdot CH_3OH$	18.6	26.3	18.4(72)	28.1(1240)
$Cu_2(pro\text{-}nno)_2$	19.5	27.2	18.1(84)	28.1(1480)
$Cu_2(hyp\text{-}nno)_2 \cdot 3/2H_2O$	18.9	27.3	17.8(69)	28.0(1160)

Conclusion

In a series of the $Cu_2(aa\text{-}nno)_2$ complexes, the variation of amino acid moiety did not affect much the magnetic and spectral properties. All the complexes have large $-2J$ values. The $Cu_2(aa\text{-}nno)_2$ complexes have the 5–6–(4)–6–5 fused chelate ring system [7] which is favorable for a planar binuclear structure. In contrast to the binuclear complexes with the diaminoalcohols, the axial ligation is hindered in the present complexes due to the larger negative charge. The resulting square planar coordination causes a very strong antiferromagnetism.

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