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Synthesis, Spectral and Magnetic Properties and Crystal Structures of Alkoxo-oxygen Coordinated Copper(II) Complexes of *N,N'*-Disubstituted Malonamide and Oxamide Derivatives

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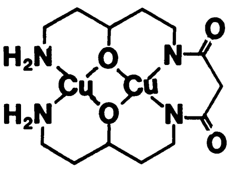
1:1 Copper(II) complexes with *N,N'*-bis(2-hydroxyethyl)malonamide (abbreviated as H_4maae), MCu(maae) (M=Ca, Sr, Ba), and 2:1 copper(II) complexes with *N,N'*-bis(5-amino-3-hydroxypentyl)malonamide and *N,N'*-bis(5-amino-3-hydroxypentyl)oxamide (abbreviated as H_4madpl and H_4oxdpl, respectively),[Cu_2(madpl)]·$3H_2O$ and [Cu_2(oxdpl)]·$2H_2O$, were prepared and characterized by elemental analyses, infrared and electronic spectra, and magnetic susceptibilities. The 2:1 complexes exhibit a band at 23.3—27.0×10^3 cm^{-1} characteristic of alkoxo-oxygen bridged structure and show a very strong antiferromagnetic interaction, whereas the 1:1 complexes show no such band and their magnetic moments fall in the range of those for ordinary mononuclear copper(II) complexes. The crystal structures of [Cu_2(madpl)]·$3H_2O$ and BaCu(maae)·$7H_2O$ were determined by the single-crystal X-ray diffraction method. The structure of [Cu_2(madpl)]·$3H_2O$ consists of alkoxo-oxygen bridged binuclear molecules, where madpl^{4-} functions as a sexadentate binucleating ligand with an $N_2O_2N_2$ donor set. In BaCu(maae)·$7H_2O$, the basic unit is a hetero-metal tetranuclear entity $(H_2O)_2\{Ba(H_2O)_4Cu(maae)\}_2$ in which the two Ba^{2+} are linked sharing two H_2O and are also bound to alkoxo oxygens of Cu(maae)$^{2-}$. On the basis of the crystal structures, their spectral properties were discussed.

Although a great number of binuclear copper(II) complexes have been prepared, only few examples containing amide nitrogen coordination are known. Recently, we reported the preparation, crystal structure, spectra and magnetic properties of binuclear copper(II) complexes of amides derived from 3-amino-1-propanol and various amino acids.[1] The deprotonated amide coordination resulted in a marked increase in the planarity of the molecule. The magnetic and spectral properties of these complexes are consistent with the planar structure. As the continuation, in this study, we have prepared new sexadentate binucleating ligands derived from the reaction of 1,5-diamino-3-pentanol and diethyl malonate or diethyl oxalate (abbreviated as H_4madpl and H_4oxdpl, respectively) and isolated their 2:1 copper(II) complexes,[Cu_2(madpl)] (**1**) and [Cu_2(oxdpl)] (**2**), respectively. We have also prepared 1:1 copper(II) complexes with *N,N'*-bis(2-hydroxyethyl)malonamide (abbreviated as H_4maae),[2] MCu(maae) (M=Ca, Sr, Ba) (**3**). These complexes were characterized by spectral and magnetic measurements. The determination of X-ray crystal structures have been carried out for [Cu_2(madpl)]·$3H_2O$ and BaCu(maae)·$7H_2O$. The former complex has been found to have an alkoxo-oxygen bridged binuclear structure as expected. On the other hand, the latter has been revealed to be composed of novel type linearly linked Cu-Ba-Ba-Cu tetranuclear entities.



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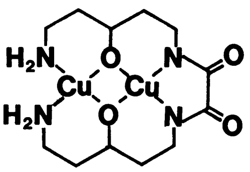

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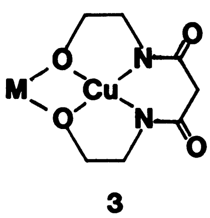

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Experimental

Preparation of the Ligands. 1,5-Diamino-3-pentanol was prepared according to the method reported by Murase *et al.*[3] The preparative methods for H_4maae,[2] H_4madpl, and H_4oxdpl are all similar and exemplified by that for H_4oxdpl.

A 2:1 mixture of 1,5-diamino-3-pentanol and diethyl oxalate in ethanol was refluxed for 2 h. A white precipitate resulted was collected by filtration and washed with ethanol. This was used for synthesis of the complex without further purification.

Preparation of the Complexes. BaCu(maae)·$7H_2O$: To a mixture of copper(II) hydroxide (250 mg), H_4maae (500 mg) and sodium hydroxide (410 mg) in 100 ml of water was added 630 mg of barium chloride dihydrate under nitrogen atmosphere. The resulting reddish purple solution was filtered and allowed to stand overnight at room temperature. Red crystals separated were collected by filtration and dried in an open air. Anal. Found: C, 16.47; H, 4.62; N, 5.56%. Calcd for BaCu(maae)·$7H_2O$: C, 16.38; H, 4.71; N, 5.46%. The crystals lost all of the crystal water in a P_2O_5 desiccator under reduced pressure. Found: C, 21.57; H, 2.76; N, 7.16; Cu, 16.84%. Calcd for BaCu(maae): C, 21.72; H, 2.60; N, 7.24; Cu, 16.42%.

SrCu(maae): This complex was obtained as purple powder in the same way as that of BaCu(maae) except for using strontium chloride hexahydrate in place of barium chloride dihydrate. Found: C, 24.63; H, 3.07; N, 8.20; Cu, 19.12%. Calcd for SrCu(maae): C, 24.92; H, 2.99; N, 8.30; Cu, 18.84%.

CaCu(maae)·$3H_2O$: This complex was obtained as purple powder in the same way as that of BaCu(maae) except for using calcium chloride dihydrate instead of barium chloride dihydrate. The product was dried in a P_2O_5 desiccator under reduced pressure for two days. Found: C, 24.47; H, 4.74; N, 8.17; Cu, 20.50%. Calcd for CaCu(maae)·$3H_2O$: C, 24.45; H, 4.69; N, 8.15; Cu, 20.38%.

[Cu_2(madpl)]·$3H_2O$: To a mixture of copper(II) hydroxide (510 mg) and H_4madpl (800 mg) in 40 ml of water was added 840 mg of sodium hydroxide to give a reddish brown solution.

The solution was filtered and concentrated under reduced pressure to precipitate a red solid. It was recrystallized from ethanol to give red plates. Found: C, 32.45; H, 6.23; N, 11.48%. Calcd for $[Cu_2(madpl)]\cdot 3H_2O$: C, 32.43; H, 6.28; N, 11.64%.

$[Cu_2(oxdpl)]\cdot 2H_2O$: This complex was obtained as brown powder in a similar manner to the above but could not be recrystallized because of its low solubility in conventional solvents. Found: C, 31.99; H, 5.77; N, 12.39; Cu, 28.16%. Calcd for $[Cu_2(oxdpl)]\cdot 2H_2O$: C, 32.07; H, 5.83; N, 12.47; Cu, 28.28%.

Measurements. Cabon, 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. 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 over the temperature range 80—300 K. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants. Effective magnetic moments were 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

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS ($\times 10^4$) AND THERMAL PARAMETERS OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2
(1) $[Cu_2(madpl)]\cdot 3H_2O$				
Cu(1)	1228(1)	3001(1)	657(1)	2.7
Cu(2)	2541(1)	2306(1)	841(1)	2.4
O(1)	1860(3)	2387(8)	−490(5)	3.2
O(2)	4018(3)	2172(9)	−1401(6)	3.8
O(3)	4075(3)	2474(8)	3314(6)	3.2
O(4)	1896(2)	2901(8)	1969(5)	3.0
OW(1)	391(4)	233(11)	1153(8)	6.1
OW(2)	5037(3)	5897(10)	1219(8)	5.3
OW(3)	4395(3)	1440(9)	5993(7)	3.8
N(1)	609(3)	3037(11)	−894(8)	3.9
N(2)	3098(3)	1856(9)	−573(7)	2.6
N(3)	3119(3)	2253(9)	2423(6)	2.5
N(4)	685(3)	3952(10)	1981(8)	3.3
C(1)	758(4)	2484(14)	−2307(9)	3.8
C(2)	1207(4)	1247(13)	−2250(9)	3.6
C(3)	1830(4)	1763(11)	−1878(8)	2.8
C(4)	2292(4)	527(11)	−1968(9)	2.9
C(5)	2911(4)	1132(11)	−1915(8)	2.9
C(6)	3646(4)	2315(10)	−452(8)	2.4
C(7)	3879(4)	3091(11)	918(9)	3.2
C(8)	3674(4)	2551(10)	2315(8)	2.5
C(9)	2958(4)	1841(12)	3863(8)	3.5
C(10)	2320(5)	1541(14)	3964(10)	4.3
C(11)	1907(4)	2806(11)	3466(8)	3.0
C(12)	1298(5)	2678(10)	3945(11)	5.2
C(13)	868(5)	3938(13)	3534(10)	4.2
(2) $BaCu(maae)\cdot 7H_2O$				
Ba	708(1)	772(1)	−2161(1)	1.9
Cu	1235(2)	3822(2)	−2908(2)	1.9
O(1)	−668(12)	2568(10)	−3376(15)	2.5
O(2)	−40(13)	6900(10)	−1727(16)	2.7
O(3)	4700(13)	6978(10)	−2106(15)	2.5
O(4)	2280(14)	2582(10)	−3213(15)	2.5
OW(1)	−1251(13)	786(9)	−356(14)	2.5
OW(2)	−1421(14)	−1590(10)	−3637(15)	2.6
OW(3)	1711(15)	−552(11)	−4258(16)	3.3
OW(4)	2157(15)	2847(13)	463(17)	3.8
OW(5)	3858(14)	841(11)	−304(16)	3.2
OW(6)	4341(16)	1535(12)	3986(18)	3.6
OW(7)	5063(21)	576(14)	−2979(20)	4.8
N(1)	180(16)	5020(13)	−2518(19)	2.6
N(2)	3127(14)	5043(12)	−2556(19)	2.3
C(1)	−1733(24)	3039(17)	−3011(38)	5.2
C(2)	−1426(21)	4351(16)	−2811(33)	4.4
C(3)	716(18)	6177(14)	−2061(20)	2.1
C(4)	2350(20)	6867(16)	−1830(28)	3.4
C(5)	3464(18)	6236(14)	−2204(20)	2.2
C(6)	4285(20)	4504(14)	−2808(25)	2.9
C(7)	3917(18)	3218(14)	−2453(22)	2.4

temperature-independent paramagnetism in cgs emu.

X-Ray Crystal Structure Analysis. *[Cu_2(madpl)]·3H_2O*: A crystal with dimensions of 0.37×0.31×0.09 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. Intensity data were collected by the 2θ-ω scan technique with a scan rate of 8 ° min^{-1}. For weak reflections the peak scan was repeated up to four times depending on their intensities. Three standard reflections were monitored after every 100 reflections, and their intensities showed a good stability. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption.

Crystal Data: $Cu_2(C_{13}H_{24}N_4O_4)\cdot 3H_2O$, F. W.=481.5, monoclinic, space group $P2_1/n$, a=22.613(21), b=8.890(7), c=9.496(5) Å, β=93.00(8) °, D_m=1.66, D_c=1.68 g cm^{-3}, Z=4.

A total of 4200 reflections with $2\theta \leq 52$ ° were collected, of

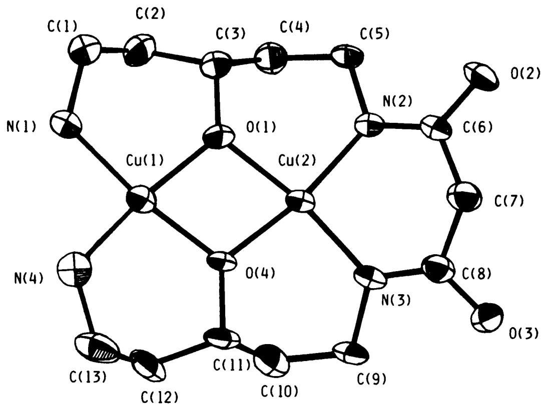

Fig. 1. Molecular structure of [Cu_2(madpl)]·3H_2O with thermal ellipsoids (50% probability level). Water molecules are not shown.

Table 2. Interatomic distances (l/Å) and bond angles (ϕ/°) with their estimated standard deviations in parentheses

(1) [Cu_2(madpl)]·3H_2O			
(a) Copper coordination spheres			
Cu(1)···Cu(2)	3.029(3)	Cu(2)-O(1)	1.940(6)
Cu(1)-O(1)	1.922(6)	Cu(2)-O(4)	1.927(6)
Cu(1)-O(4)	1.910(6)	Cu(2)-N(2)	1.930(7)
Cu(1)-N(1)	1.978(8)	Cu(2)-N(3)	1.940(6)
Cu(1)-N(4)	1.990(8)		
Cu(1)-O(1)-Cu(2)	103.3(3)	N(1)-Cu(1)-N(4)	91.6(3)
Cu(1)-O(4)-Cu(2)	104.3(2)	O(1)-Cu(2)-O(4)	75.8(2)
O(1)-Cu(1)-O(4)	76.7(2)	O(1)-Cu(2)-N(2)	94.5(3)
O(1)-Cu(1)-N(1)	95.8(3)	O(4)-Cu(2)-N(3)	94.3(3)
O(4)-Cu(1)-N(4)	95.8(3)	N(2)-Cu(2)-N(3)	95.5(3)
(b) Madpl moiety			
N(1)-C(1)	1.484(12)	C(7)-C(8)	1.506(12)
C(1)-C(2)	1.496(15)	O(3)-C(8)	1.280(10)
C(2)-C(3)	1.506(13)	N(3)-C(8)	1.292(11)
O(1)-C(3)	1.428(10)	N(3)-C(9)	1.480(11)
C(3)-C(4)	1.522(13)	C(9)-C(10)	1.474(15)
C(4)-C(5)	1.499(13)	C(10)-C(11)	1.521(15)
N(2)-C(5)	1.469(11)	O(4)-C(11)	1.423(9)
N(2)-C(6)	1.306(11)	C(11)-C(12)	1.477(14)
O(2)-C(6)	1.270(10)	C(12)-C(13)	1.522(17)
C(6)-C(7)	1.541(12)	N(4)-C(13)	1.511(12)
Cu(1)-N(1)-C(1)	118.9(6)	N(3)-C(8)-C(7)	118.8(7)
N(1)-C(1)-C(2)	113.3(8)	O(3)-C(8)-C(7)	115.5(7)
C(1)-C(2)-C(3)	114.1(9)	O(3)-C(8)-N(3)	125.7(7)
O(1)-C(3)-C(2)	109.5(7)	Cu(2)-N(3)-C(8)	123.5(5)
Cu(1)-O(1)-C(3)	129.2(5)	Cu(2)-N(3)-C(9)	122.3(6)
C(2)-C(3)-C(4)	113.8(8)	C(8)-N(3)-C(9)	114.3(7)
O(1)-C(3)-C(4)	109.4(7)	N(3)-C(9)-C(10)	113.2(7)
Cu(2)-O(1)-C(3)	125.8(5)	C(9)-C(10)-C(11)	115.7(9)
C(3)-C(4)-C(5)	112.4(8)	O(4)-C(11)-C(10)	109.4(7)
N(2)-C(5)-C(4)	114.3(7)	Cu(2)-O(4)-C(11)	124.4(5)
Cu(2)-N(2)-C(5)	121.7(5)	C(10)-C(11)-C(12)	114.5(9)
C(5)-N(2)-C(6)	116.2(7)	O(4)-C(11)-C(12)	110.2(7)
Cu(2)-N(2)-C(6)	121.7(5)	Cu(1)-O(4)-C(11)	128.8(5)
N(2)-C(6)-C(7)	119.7(7)	C(11)-C(12)-C(13)	117.3(10)
O(2)-C(6)-N(2)	124.6(7)	N(4)-C(13)-C(12)	113.3(9)
O(2)-C(6)-C(7)	115.8(7)	Cu(1)-N(4)-C(13)	117.9(6)
C(6)-C(7)-C(8)	119.6(8)		
(c) Hydrogen bonds			
OW(1)···OW(1)$^{\mathrm{ia)}}$	2.774(12)	OW(1)···N(1)	3.215(13)
OW(1)···OW(3)$^{\mathrm{ii}}$	2.493(12)	OW(1)···N(4)	3.455(13)
OW(1)···O(3)$^{\mathrm{iii}}$	2.728(12)	OW(2)···N(4)$^{\mathrm{v}}$	2.429(11)
OW(1)···OW(3)$^{\mathrm{iii}}$	2.589(11)		
OW(2)···O(2)$^{\mathrm{iv}}$	2.739(11)		
OW(2)···OW(2)$^{\mathrm{iv}}$	2.809(12)		

TABLE 2. (Continued)

(2) BaCu(maae)·7H_2O			
(a) Barium coordination spheres			
Cu···Ba	3.569(2)	Ba-OW(2)	2.794(10)
Ba-O(1)	2.777(12)	Ba-OW(3)	2.811(16)
Ba-O(4)	2.741(13)	Ba-OW(4)	2.757(12)
Ba-OW(1)	2.889(15)	Ba-OW(5)	2.827(13)
Ba-OW(1)$^{\mathrm{i}}$[a]	2.960(12)		
O(1)-Ba-O(4)	60.6(4)	OW(1)-Ba-OW(2)	79.4(4)
O(1)-Ba-OW(1)	80.3(4)	OW(1)-Ba-OW(3)	149.5(3)
O(1)-Ba-OW(2)	110.8(3)	OW(1)-Ba-OW(4)	72.7(4)
O(1)-Ba-OW(3)	117.1(4)	OW(1)-Ba-OW(5)	117.8(4)
O(1)-Ba-OW(4)	74.6(4)	OW(2)-Ba-OW(3)	71.1(4)
O(1)-Ba-OW(5)	132.4(3)	OW(2)-Ba-OW(4)	150.2(5)
O(4)-Ba-OW(1)	132.9(4)	OW(2)-Ba-OW(5)	115.6(4)
O(4)-Ba-OW(2)	136.6(4)	OW(3)-Ba-OW(4)	131.1(4)
O(4)-Ba-OW(3)	76.5(4)	OW(3)-Ba-OW(5)	70.5(4)
O(4)-Ba-OW(4)	72.4(4)	OW(4)-Ba-OW(5)	70.8(4)
O(4)-Ba-OW(5)	78.2(4)	OW(1)$^{\mathrm{i}}$-Ba-OW(5)	63.8(4)
OW(1)-Ba-OW(1)$^{\mathrm{i}}$	67.1(4)	Ba-OW(1)-Ba$^{\mathrm{i}}$	112.9(4)
(b) Copper coordination spheres			
Cu-O(1)	1.918(11)	Cu-N(1)	1.943(17)
Cu-O(4)	1.955(14)	Cu-N(2)	1.923(13)
O(1)-Cu-O(4)	91.8(5)	O(4)-Cu-N(2)	86.6(6)
O(1)-Cu-N(1)	86.7(6)	N(1)-Cu-N(2)	94.9(6)
(c) Maae moiety			
O(1)-C(1)	1.382(31)	C(4)-C(5)	1.526(30)
C(1)-C(2)	1.431(26)	O(3)-C(5)	1.265(20)
N(1)-C(2)	1.473(25)	N(2)-C(5)	1.292(20)
N(1)-C(3)	1.254(20)	N(2)-C(6)	1.457(27)
O(2)-C(3)	1.289(24)	C(6)-C(7)	1.528(24)
C(3)-C(4)	1.520(25)	O(4)-C(7)	1.428(18)
Cu-O(1)-Ba	97.3(4)	N(2)-C(5)-C(4)	120.6(16)
Cu-O(1)-C(1)	112.8(9)	O(3)-C(5)-N(2)	125.3(18)
Ba-O(1)-C(1)	130.2(14)	O(3)-C(5)-C(4)	114.1(14)
O(1)-C(1)-C(2)	114.5(21)	Cu-N(2)-C(5)	129.1(14)
N(1)-C(2)-C(1)	114.7(19)	Cu-N(2)-C(6)	113.3(10)
Cu-N(1)-C(2)	108.8(11)	C(5)-N(2)-C(6)	117.5(14)
Cu-N(1)-C(3)	128.4(14)	N(2)-C(6)-C(7)	104.8(16)
C(2)-N(1)-C(3)	122.8(17)	O(4)-C(7)-C(6)	112.9(13)
N(1)-C(3)-C(4)	122.7(18)	Cu-O(4)-Ba	97.5(6)
O(2)-C(3)-N(1)	124.2(17)	Ba-O(4)-C(7)	127.6(10)
O(2)-C(3)-C(4)	113.1(13)	Cu-O(4)-C(7)	106.0(9)

a) Symmetry code

Superscript	
i	$-x, -y, -z$
ii	$x-1/2, y, z-1/2$
iii	$1/2-x, -y, 1/2-z$
iv	$1-x, 1-y, -z$
v	$1/2-x, 1-y, 1/2-z$

which independent 2596 reflections had $|F_o| \geq 3\sigma(F_o)$ and were employed in the solution and refinement of the structure.

The structure was solved by the heavy-atom method. Refinement was carried out by the block-diagonal least-squares method. All the hydrogen atoms except for those of the water molecules were located from the difference Fourier map and included in the refinement. The final *R* value was 0.067.

BaCu(maae)·7H₂O: Data collection from a crystal of dimensions of 0.40×0.30×0.28 mm was carried out in a fashion similar to that employed for Cu_2(madpl)·3H_2O.

Crystal Data: BaCu($C_7H_{10}N_2O_4$)·7H_2O, F. W.=513.2, triclinic space group $P\bar{1}$, a=9.642(3), b=11.374(3), c=8.761(3) Å, α=96.93(2), β=112.27(2), γ=102.83(2)°, D_m=2.02, D_c=2.02 g cm^{-3}, Z=2.

A total of 3746 reflections with $2\theta \leq 52°$ were collected, of which independent 3184 reflections had $|F_o| \geq 3\sigma(F_o)$ and were used in the solution and refinement of the structure. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All the hydrogen atoms except for those bound to the water oxygen atoms, OW(2), OW(3), OW(4), and OW(5), were located from the difference Fourier map and included in the refinement. The final *R* value was 0.080.

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[4] of the UNICS-III and the ORTEP programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 1. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the nonhydrogen atoms, and the F_o-F_c tables have been deposited as a Document No. 8428 at the Office of the Editor.

Results and Discussion

Description of the Structure. *[Cu_2(madpl)]·3H_2O*: The crystal consists of alkoxo-oxygen bridged binuclear molecules, [Cu_2(madpl)], and crystal water. A perspective drawing of the binuclear molecule and the numbering system are illustrated in Fig. 1. Bond lengths and angles are listed in Table 2.

The two copper atoms, Cu(1) and Cu(2), are bridged by two alkoxo-oxygen atoms of madpl, O(1) and O(4). The N_2O_2 donor sets are planar and Cu(1) and Cu(2) deviate from the relevant N_2O_2 planes only by 0.081 and 0.018 Å, respectively. The dihedral angle of the planes is 7.4 °. The Cu-O bond lengths (1.910—1.940 Å) and the Cu-N (amine) bond lengths (1.978(8) and 1.990(8) Å) are normal for in-plane coordination.[5–7] The Cu-N (amide) distances (1.930(7) and 1.940(6) Å) are substantially shorter than the Cu-N (amine) distances and fall in the range of those of deprotonated amide complexes (1.89—1.99 Å, average 1.92 Å).[8]

In the madpl moiety, the C-N bond lengths of the amide bonds (1.306(11) and 1.292(11) Å) are shorter than the other C-N bond distances (1.469—1.511 Å) as found in many copper(II) complexes with deprotonated amides.[8] The madpl ligand forms five six-membered chelate rings with two copper atoms. All these chelate rings assume a boat conformation (Table 3). The bonds attached to the bridging oxygen atom are almost coplanar (sums of the bond angles subtended at O(1) and O(3) are 358.3 and 357.5 °, respectively).

The water molecules are located in the vicinity of

Table 3. Coefficients of equations of mean planes and deviations of atoms from the planes

	l	m	n	d	Distances from the planes (l/Å)			
(1) [Cu_2(madpl)]·3H_2O								
(a) Plane through O(1), O(4), N(1), N(4)	0.2703	0.9328	−0.2521	3.1635	O(1)	0.070	O(4)	−0.071
					N(1)	−0.059	N(4)	0.059
					Cu(1)	−0.081		
(b) Plane through O(1), O(4), N(2), N(3)	0.1926	0.9708	−0.1531	2.9921	O(1)	−0.051	O(4)	0.051
					N(2)	0.042	N(3)	−0.042
					Cu(2)	−0.018		
(c) Plane through O(4), N(3), C(9), C(11)	0.2324	0.9523	0.1853	3.8878	O(4)	−0.089	N(3)	0.085
					C(9)	−0.095	C(11)	0.100
					Cu(2)	−0.453	C(10)	−0.666
(d) Plane through O(4), N(4), C(11), C(13)	0.3542	0.9352	−0.0236	3.8371	O(4)	0.049	N(4)	−0.047
					C(11)	−0.055	C(13)	0.053
					Cu(1)	−0.373	C(12)	−0.659
(e) Plane through O(1), N(2), C(3), C(5)	0.1633	0.8864	−0.4412	2.8100	O(1)	−0.037	N(2)	0.036
					C(3)	0.042	C(5)	−0.041
					Cu(2)	−0.408	C(4)	−0.724
(f) Plane through O(1), N(1), C(1), C(3)	0.2592	0.9117	−0.3319	3.1394	O(1)	0.040	N(1)	−0.039
					C(1)	0.045	C(3)	−0.046
					Cu(1)	−0.194	C(2)	−0.713
(g) Plane through N(2), N(3), C(6), C(8)	−0.2586	0.9599	−0.0944	−0.1475	N(2)	−0.029	N(3)	0.029
					C(6)	0.031	C(8)	−0.032
					Cu(2)	0.554	C(7)	0.434
(h) Plane through Cu(1), Cu(2), C(3)	0.2121	0.9316	−0.3060	2.8835	Cu(1)	0.000	Cu(2)	0.000
					C(3)	0.000	O(1)	0.128
(i) Plane through Cu(1), Cu(2), C(11)	0.2069	0.9773	−0.0554	3.1476	Cu(1)	0.000	Cu(2)	0.000
					C(11)	0.000	O(4)	0.156
(j) Plane through Cu(1), Cu(2), O(1), O(4)	0.2114	0.9599	−0.1950	3.0218	Cu(1)	0.005	Cu(2)	0.005
					O(1)	−0.005	O(4)	−0.005
					C(3)	−0.294	C(11)	−0.358
(2) BaCu(maae)·7H_2O								
(a) Plane through O(1), O(4), N(1), N(2)	−0.0162	−0.2165	0.9314	−3.3350	O(1)	−0.042	O(4)	0.042
					N(1)	0.041	N(2)	−0.041
					Cu	0.001	Ba	1.370
(b) Plane through Cu, O(1), N(1)	−0.0170	−0.2461	0.9313	−3.4629	Cu	0.000	O(1)	0.000
					N(1)	0.000	C(1)	0.184
					C(2)	−0.026		
(c) Plane through Cu, O(4), N(2)	−0.0153	−0.1869	0.9306	−3.2018	Cu	0.000	O(4)	0.000
					N(2)	0.000	C(6)	−0.109
					C(7)	0.460		
(d) Plane through Cu, N(1), N(2), C(3), C(4), C(5)	0.0300	−0.2540	0.9133	−3.4206	Cu	0.025	N(1)	−0.039
					N(2)	0.010	C(3)	0.008
					C(4)	0.040	C(5)	−0.044
					O(2)	0.044	O(3)	−0.144
(e) Plane through Ba, Cu, C(1)	−0.0834	0.1787	0.8829	−1.5721	Ba	0.000	Cu	0.000
					C(1)	0.000	O(1)	−0.465
(f) Plane through Ba, Cu, C(7)	−0.0887	0.1798	0.8846	−1.5778	Ba	0.000	Cu	0.000
					C(7)	0.000	O(4)	−0.579

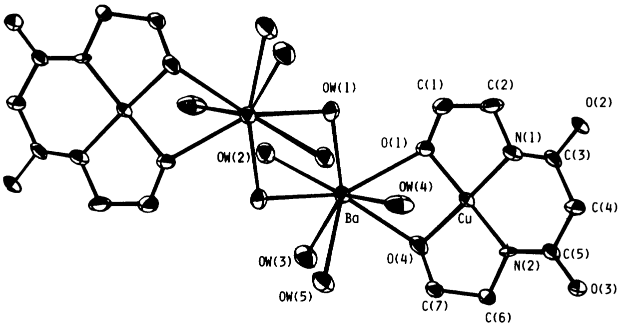

Fig. 2. A perspective view of BaCu(maae)·7H_2O with thermal ellipsoids (50% probability level).

the amino and carbonyl groups of the madpl ligand by hydrogen bonding (Table 2) and do not coordinate to the copper atoms.

BaCu(maae)·7H_2O: The molecular structure of BaCu(maae)·7H_2O is shown in Fig. 2. The unit cell contains two BaCu(maae)·5H_2O units and crystal water molecules. Two water molecules intervene between two barium atoms to form a Cu-Ba-Ba-Cu tetranuclear entity as shown in Fig. 2. This unit is located at the crystallographic inversion center.

Each copper atom is coordinated by two alkoxo-oxygen and two amide nitrogen atoms in a square-planar geometry. These donor atoms are almost coplanar with the largest deviation of 0.042 Å, and the copper atom deviates from this plane by 0.001 Å. The Cu-O bond lengths (1.918(11) and 1.955(14) Å) fall in the range of those of the alkoxo-oxygen bridged binuclear copper(II) complexes.[1,5-7] The Cu-N (1.943(17) and 1.923(13) Å), C=O (1.289(24) and 1.265(20) Å) and C-N 1.254(20) and 1.292(20) Å) distances of the amide bonds are normal for the bond lengths of copper(II) complexes with deprotonated amides.[8] In the IR spectrum, the amide I (at≈1630 cm^{-1}) and amide II[9] (at≈1560 cm^{-1}) bands of the H_4maae are replaced by the band at≈1595 cm^{-1} on coordination. This is in accord with the general rule for the deprotonated amide coordination.[1]

The six-membered Cu-N(1)-C(3)-C(4)-C(5)-N(2) chelate ring is planar, the maximum deviation from the least-squares plane being 0.044 Å. The two five-membered Cu-O(1)-C(1)-C(2)-N(1) and Cu-O(4)-C(7)-C(6)-N(2) chelate rings assume a gauche conformation as is usually observed for saturated five-membered chelate rings.

The coordination around the barium atom is a distorted square antiprism with two alkoxo-oxygen atoms from the maae ligand and six water oxygen atoms. The barium-oxygen distances vary from 2.741 to 2.960 Å. These values are in the normal range for an eight-coordinated barium ion.[10] The Ba-O(1) and Ba-O(4) bond lengths are substantially shorter than the Ba-O (water oxygen) distances. The barium atom is not in the coordination plane of Cu(maae), the deviation from the O(1)-O(4)-N(1)-N(2) plane being 1.37 Å (Table 3). The geometries around the alkoxo-oxygen atoms considerably deviate from planar arrangement (sums of the bond angles subtended at O(1) and O(4) are 340.3 and 331.1 °, respectively).

Electronic Spectra. Some examples of the electronic spectra in nujol mull are shown in Fig. 3. The band maxima are given in Table 4.

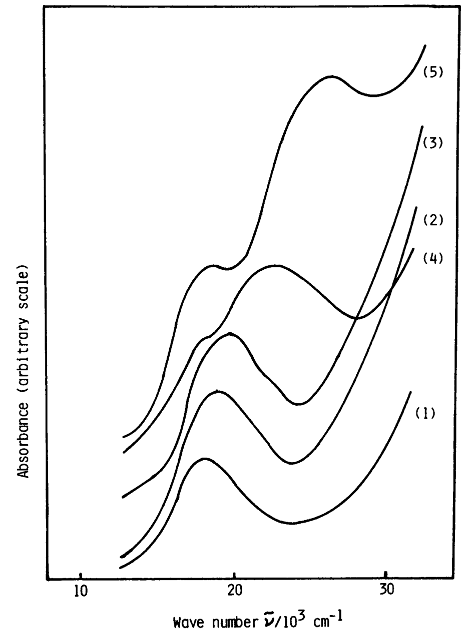

Fig. 3. Electronic spectra of (1) CaCu(maae)·3H_2O, (2) SrCu(maae), (3) BaCu(maae), (4) [Cu_2(oxdpl)]·2H_2O, and (5) [Cu_2(madpl)]·3H_2O in nujol mull.

TABLE 4. SPECTRAL DATA

Complex	Nujol mull spectra $\tilde{\nu}_{max}/10^3$ cm^{-1}	
[Cu_2(madpl)]·3H_2O	19.0	27.0
	18.2(97)	27.8(1260)[a)]
[Cu_2(oxdpl)]·2H_2O	18 sh[b)]	23.3
BaCu(maae)	19.8	
BaCu(maae)·7H_2O	18.8	
SrCu(maae)	19.2	
CaCu(maae)·3H_2O	18.5	

a) Absorption spectra in aqueous solution($\tilde{\nu}_{max}/10^3$ cm^{-1} (ε)). b) sh=shoulder.

All the complexes show a band assignable to d-d transitions at 18.5—19.8×10^3 cm^{-1}. The relatively high values of $\tilde{\nu}_{max}$ considered from the N_2O_2 coordination environment may be attributed to the square-planar coordination free from the axial perturbation.[1] More intense bands were observed at 27.0×10^3 and 23.3×10^3 cm^{-1} for [Cu_2(madpl)]·3H_2O and [Cu_2(oxdpl)]·2H_2O, respectively. On the other hand, in the MCu(maae) complexes, no such bands were observed in this region. It is known that alkoxo-oxygen bridged binuclear copper(II) complexes always show an absorption at 22—29×10^3 cm^{-1}. This band is characteristic of alkoxo-oxygen bridged structure and may be assigned to $p_\pi(O) \rightarrow d(Cu)$ charge transfer transition.[11-13] The absence and presence of the characteristic CT band in the present complexes are understandable in terms of their bonding mode of the bridging oxygen atoms. The X-ray structure analyses of [Cu_2(madpl)]·3H_2O and BaCu(maae)·

Table 5. Magnetic data

Complex	μ_{eff}/B.M. (T/K)	θ/K	$2J$/cm^{-1} [a)]	$N\alpha\times10^6$/cgs emu	P
[Cu_2(madpl)]·$3H_2O$	0.36 (293)		−1075	27	0.017
[Cu_2(oxdpl)]·$2H_2O$	0.55 (298)		−855	60	0.020
BaCu(maae)	1.71 (291)	−5			
SrCu(maae)	1.75 (288)	−5			
CaCu(maae)·$3H_2O$	1.83 (295)	−12			

a) For all the complexes g=2.10 was assumed.

$7H_2O$ show that both complexes have alkoxo-oxygen bridged structures, but the two structures differ in their bridging mode: in [Cu_2(madpl)]·$3H_2O$ the bonds attached to the bridging oxygen are almost coplanar as found for alkoxo-oxygen bridged binuclear copper(II) complexes so far reported,[1,5–7] whereas in BaCu(maae)·$7H_2O$ the geometry around the alkoxo-oxygen atom considerably deviates from planar arrangement. This fact suggests that a planar structure of the bridging oxygen may be responsible for the appearence of the characteristic band. Kida *et al.* interpreted the $p_\pi(O)\rightarrow d(Cu)$ charge transfer band in the visible region in the following way.[12] Usually the nonbonding orbital on the alkoxo-oxygen atom should be regarded to be sp^3 hybridized orbital rather than a p_z orbital. However, in the case of the bridging oxygen in a planar binuclear-structure, the good planarity of the  $\begin{array}{c}\mathrm{Cu}\quad\mathrm{Cu}\\ \diagdown\mathrm{O}\diagup\\ |\\ \mathrm{C}\end{array}$ bond would result in a pure p-character of the nonbonding orbital of the alkoxo-oxygen atom. Since optical electronegativity of the nonbonding electrons is dependent on the degree of hybridization of 2s and 2p orbitals, the O→Cu charge transfer band for the planar binuclear-structure would be lower in frequency compared with those of the usual nonplanar alkoxo complexes such as BaCu(maae)·$7H_2O$.

Magnetic Susceptibilities. The magnetic moments of the MCu(maae) complexes are 1.71—1.83 B. M. at room temperature. These complexes obey the Curie-Weiss law, $\chi_A=C/(T-\theta)$, in the temperature range 80—300 K. The Weiss constants, θ, are given in Table 5. The small negative θ values indicate that a weak antiferromagnetic interaction is operative between the copper(II) ions.

The magnetic moments per copper atom of [Cu_2(madpl)]·$3H_2O$ and [Cu_2(oxdpl)]·$2H_2O$ are 0.36 and 0.55 B. M., respectively, at room temperature, indicating a strong antiferromagnetic interaction is operating between the copper (II) ions. The temperature dependence of magnetic susceptibilities for these complexes can be interpreted by the modified Bleaney-Bowers equation[14]

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

where χ_A is a 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 Eq. 1 was added to account for the presence of a small amount of paramagnetic impurity. The parameters, $-2J$, $N\alpha$, and P were evaluated from the best fit of the experimental data to Eq. 1 and are listed in Table 5. It is notable that the $-2J$ values, the energy separation between the spin-singlet ground state and the lowest spin-triplet state, for the present binuclear complexes are very large. Generally an antiferromagnetic spin-exchange interaction between two copper(II) ions becomes stronger when the tetragonal planes of the two copper(II) ions become more coplanar. In [Cu_2(madpl)]·$3H_2O$, the two copper(II) ions and the donating atoms are almost coplanar, and there is no axial coordination which is a factor of depressing the antiferromagnetic interaction. Therefore, the very strong antiferromagnetic interaction observed for the present binuclear copper(II) complexes is attributable to the planar skeleton.[1)]

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