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Polynuclear Complexes with Hydrogen-Bonded Bridges. 4. Structure and Magnetic Properties of Dinuclear Copper(II) Complexes of Amino Alcohols[1]

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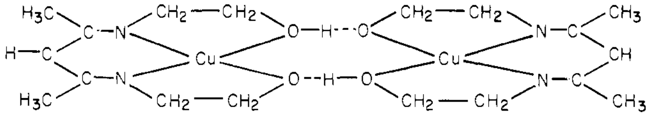
The structures and magnetic properties of the copper(II) complexes of 2-aminoethanol (EtaH), $[Cu(EtaH)(Eta)]_2(NO_3)_2$, and 2-amino-2-methylpropanol (MepH), $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$, have been investigated. The compound $[Cu(EtaH)(Eta)]_2(NO_3)_2$ crystallizes in space group $P\bar{1}$ ($a = 9.990$ (2) Å, $b = 11.454$ (1) Å, $c = 9.977$ (2) Å, $\alpha = 111.10$ (1)°, $\beta = 90.02$ (1)°, and $\gamma = 119.92$ (1)° at 25 °C with Mo Kα radiation) with 2 formula units per unit cell ($\rho_{calcd} = 1.816$ g cm^{-3}, ρ_{obsd} 1.823 g cm^{-3}), and the structure was refined to a conventional R value of 0.049 by full-matrix least-squares refinement. The structure consists of two independent dinuclear cations and uncoordinated nitrate anions; each dinuclear cation is made up of two *cis*-bis(2-aminoethanolato)copper(II) complexes related by inversion symmetry and joined by two hydrogen bonds (oxygen–oxygen distances of 2.43–2.45 Å). The compound $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$ crystallizes in space group $P2_1/c$ ($a = 6.232$ (1) Å, $b = 14.036$ (4) Å, $c = 17.097$ (4) Å, $\beta = 105.79$ (2)°) with 2 formula units per unit cell ($\rho_{calcd} = 1.481$ g cm^{-3}, $\rho_{obsd} = 1.476$ g cm^{-3}), and the structure was refined to a conventional R value of 0.041 by full-matrix least-squares refinement. The structure contains a dinuclear cation made up of two square-pyramidal copper(II) complexes related by inversion symmetry and joined by two hydrogen bonds (oxygen–oxygen distance of 2.516 (3) Å). Both compounds show antiferromagnetic coupling ($2J$ values of -56 cm^{-1} and -70 cm^{-1} for the EtaH and MepH compounds, respectively) that is weaker than that observed for the hydrogen-bonded (oxygen–oxygen distance of 2.31 Å) complex of copper(II) and the diimine of 2,4-pentanedione and 2-aminoethanol ($2J = -94$ cm^{-1}). There is no direct correlation of coupling constants with either oxygen–oxygen distances or copper–copper distances for these compounds.

Introduction

Cooperative hydrogen bonding,[2] in which molecules are joined by two or more hydrogen bonds, is possible for molecules which contain both hydrogen-bond donor groups and hydrogen-bond acceptor groups. This type of bonding is well-known in carboxylic acid dimers and was suggested[3] to explain the stoichiometry of the cobalt(III) complex of 2-aminoethanol, $[Co_2(EtaH)_3(Eta)_3]^{3+}$ (where EtaH represents 2-aminoethanol and Eta represents the corresponding anion). A structure study of $[Cu(Eph)_2]_3{\cdot}2C_6H_6$ (where Eph represents the anion of *l*-ephedrine, a substituted 2-aminoethanol) revealed[4] trimeric units $[Cu(Eph)_2]_3$ held together by nitrogen–oxygen hydrogen bonds and provided the first documented example of cooperative hydrogen bonding in transition-metal complexes. More recently, structure studies have provided examples of cooperative oxygen–oxygen hydrogen bonding in copper(II),[5,6] nickel(II),[8] nickel(II)–cobalt(III),[7] and cobalt(III)[8] dinuclear complexes.

The complex $[Cu(DiimH)]_2$ (I) of copper(II) and the diimine formed from 2,4-pentanedione and 2-aminoethanol is of particular interest because of the very short oxygen–oxygen distances (2.31 Å) and because of the spin coupling that causes the magnetic moment per gram-atom of copper to drop from 1.69 μ_B at 298 K to 1.14 μ_B at 77 K. This antiferromagnetic behavior is consistent with a singlet–triplet separation, $2J$, of -95 cm^{-1} for the dimer.



I

Because of the copper–copper distance (~5.00 Å), direct exchange is unlikely and the coupling probably occurs by superexchange through the hydrogen-bonded bridges. The magnitude of the coupling should depend on the extent of covalent bonding through these bridges and would, thus, be expected to vary inversely with the donor–acceptor distance. Since $[Cu(DiimH)]_2$ contains the shortest hydrogen-bonded oxygen–oxygen distance reported, the observed coupling constant of -95 cm^{-1} may be an upper limit for such interactions. $[Cu(Eph)_2]_3$, on the other hand, has a normal nitrogen–oxygen distance (2.87 Å) for hydrogen bonding and would be expected to show weaker coupling. Another compound, reported[9] as $Cu(EtaH)(Eta)(NO_3)$, contains alcohol, amine, and alkoxide groups and could contain either nitrogen–oxygen hydrogen bonds, as in $[Cu(Eph)_2]_3$, or oxygen–oxygen hydrogen bonds, as in $[Cu(DiimH)]_2$.

In order to investigate the relationship between structures and magnetic properties of hydrogen-bonded complexes, we have repeated the preparation of $Cu(EtaH)(Eta)NO_3$ and have prepared an analogous compound with 2-amino-2-methylpropanol (abbreviated MepH in formulas). We have determined the structures of these compounds, and we have studied the temperature dependence of their magnetic susceptibilities. Since these compounds were found to contain dinuclear, hydrogen-bonded cations, they are best presented as $[Cu(LH)L]_2(NO_3)_2{\cdot}nH_2O$, where LH represents the aminoalkoxide, L is the corresponding anion, and $n = 0$ (EtaH complex) or 2 (MepH complex). The temperature dependence of the magnetic susceptibility of $[Cu(Eph)_2]_3{\cdot}2C_6H_6$ was also investigated. The results of these studies are reported in this paper.

Experimental Section

Preparation of $[Cu(EtaH)(Eta)]_2(NO_3)_2$. This compound was prepared by a slight modification of the published method.[9] To 2.0 g (8.3 mmol) of $Cu(NO_3)_2{\cdot}3H_2O$ in 10 mL of dry methanol was added 2.7 g (44.2 mmol) of 2-aminoethanol in 16 mL of dry methanol. The

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Table I. Effective Magnetic Moments (μ_{eff}) of the Compounds

compd	μ_{eff}/g-atom of copper, μ_B		
	298 K	195 K	93 K
$[Cu(EtaH)(Eta)]_2(NO_3)_2$	1.78	1.74	1.59
$[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$	1.85	1.77	1.57
$[Cu(Eph)_2]_3 \cdot 2C_6H_6$	1.75	1.76	1.75

mixture was heated, filtered, and set aside to cool. After 1 week, the large, blue, prismatic crystals which formed were filtered and washed with absolute ethanol. Anal. Calcd for $CuC_4H_{13}N_3O_5$: C, 19.47; H, 5.31; N, 17.03. Found: C, 19.44; H, 5.31; N, 17.09.

Preparation of $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$. To a solution of 4.0 g (16.6 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 mL of a mixed solvent (acetone–ethanol = 2:1) was added 8.0 g (89.9 mmol) of 2-amino-2-methyl-1-propanol (abbreviated MepH). The resulting solution was filtered to remove thin violet plates and kept for 2 days. The blue, prismatic crystals which formed were filtered by suction and washed with ethanol. Anal. Calcd for $CuC_8H_{23}N_3O_6$: C, 29.94; H, 7.23; N, 13.10. Found: C, 30.16; H, 7.20; N, 13.15.

Preparation of $[Cu(Eph)_2]_3 \cdot 2C_6H_6$. This compound was prepared by the published method.[4] To a solution of 5.0 g (20 mmol) of $CuSO_4 \cdot 5H_2O$ and 4.0 g (26.1 mmol) of *l*-ephedrine in 100 mL of water was added 20 mL of 20% aqueous NaOH. The resulting blue slurry was extracted with benzene to give a violet solution. This benzene solution was then dried with Na_2SO_4. Repeated evaporation and crystallization of benzene solutions removed traces of water, and hexagonal platelets were obtained. For identification, the space group and cell parameters were determined and were found to be identical with the reported values.

Magnetic Susceptibility Measurements. The magnetic susceptibilties of all three compounds were determined at temperatures from 93 K to room temperature by the Faraday method using $HgCo(CNS)_4$ as calibrant. Diamagnetic corrections were made by using published atomic values.[10] The magnetic moments and susceptibilities at various temperatures are presented in Table I and Table IX, respectively.

X-ray Data Collection. A crystal with the approximate dimensions shown in Table II was mounted on a glass fiber by using epoxy cement or nail polish such that the longest dimension was approximately parallel to the fiber axis.

Unit cell parameters and orientation matrices were determined on a Syntex $P2_1$ four-circle diffractometer equipped with a graphite monochromator (Bragg 2θ angle = 12.2° using Mo $K\alpha$ radiation at a takeoff angle of 6.75°). Fifteen reflections whose 2θ values ranged from 5.00 to 25.00° were machine-centered and used in least-squares refinement of the lattice parameters and orientation matrix. Axial photographs were taken to check for mirror symmetry. Intensity data for zero and upper levels were collected at a rapid scan and the intensities examined carefully for systematic absences. The unit cell parameters and space groups obtained are shown in Table II. The calculated densities of these compounds agree well with the experimental densities, measured by the flotation method, listed in Table II. ω scans of several low 2θ angle reflections gave peak widths at half-height; indicating a satisfactory mosaic spread for the crystals. Intensity data for these complexes were collected by using θ–2θ scans with X-ray source and monochromator settings identical with those used for determination of the unit cell parameters. A variable scan rate of from 3.5 to 29.3° min^{-1} was used and a scan width of 2.00 or 2.40° was sufficient to collect all the peak intensity. Stationary-background counts were measured at the beginning (bgd1) and at the end (bgd2) of each scan with a total background to scan time ratio of 1. There were no significant fluctuations in the intensities of three standard reflections monitored every 97 reflections in the case of $[Cu(EtaH)(Eta)]_2(NO_3)_2$. Appropriate corrections were applied for the data set $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot H_2O$ where marked decomposition occurred. Intensities were calculated from the total scan count, CT, and background counts by the relationship

$$I = \text{CT} - (\text{bgd1} + \text{bgd2})$$

Table II. Crystallographic Data for the Compounds

	$[Cu(EtaH)(Eta)]_2$-$(NO_3)_2$	$[Cu(MepH)(Mep)]_2$-$(NO_3)_2 \cdot 2H_2O$
space group	$P\bar{1}$ (No. 2)[11]	$P2_1/c$ (No. 14)[11]
a, Å	9.990 (2)[12]	6.232 (1)
b, Å	11.454 (1)	14.036 (4)
c, Å	9.977 (2)	17.097 (4)
α, deg	111.10 (1)	
β, deg	90.02 (1)	105.79 (2)
γ, deg	119.92 (1)	
V, Å^3	901.8 (2)	1439.1 (6)
ρ_{calcd}, g cm^{-3}	1.816	1.481
ρ_{obsd}, g cm^{-3}	1.823	1.476
Z	2	2
cryst size, mm	0.57 × 0.22 × 0.17	0.94 × 0.36 × 0.18
range of 2θ, deg	0–50	0–60
no. of unique data	3398	4513
no. of data, $I > 3\sigma(I)$	2803	2362
no. of variables	260	225
R	0.049	0.041
R_w	0.056	0.030
largest residual peak, e/Å^3		0.32

The intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\text{CT} + (\text{bgd1} + \text{bgd2})]^{1/2}$$

From the total reflections collected out to $2\theta = 50.0°$, the numbers of reflections in the last row of Table II are the numbers accepted as statistically above background on the basis that I was greater than $3\sigma(I)$. Lorentz and polarization corrections were made in the usual way; no corrections were made for absorption (μ is 12.6 and 8.0 for $[Cu(EtaH)(Eta)]_2(NO_3)_2$ and $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$, respectively).

All computations were carried out on a CDC Cyber 70/74 computer.[13]

In the structure factor calculations, the scattering factors were taken from Cromer and Waber's tabulation[14] for all atoms except hydrogen; Stewart's hydrogen atom scattering factors were used.[15] The scattering factors for copper and chlorine were correct for the real and imaginary anomalous dispersion components, using the dispersion factors tabulated by Cromer.[16] The agreement factors are defined in the usual way as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

and

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}$$

In all least-squares refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$.

Solution and Refinement of the Structures. The structures were solved from three-dimensional Patterson functions. After refinement of heavy-atom positions, the positions of the remaining nonhydrogen atoms were located by means of Fourier syntheses.

For $[Cu(EtaH)(Eta)]_2(NO_3)_2$, two nitrate nitrogen atoms were in special positions on inversion centers at (0, 0, 0) and ($^1/_2$, 0, $^1/_2$). For these nitrates, atom multipliers of 0.5 were assigned to all atoms since the nitrogen atoms occupied special positions and the oxygen atoms were disordered by the inversion symmetry. After several cycles of refinement with anisotropic temperature factors for all atoms except the nitrates in special positions ($R = 0.07$, $R_w = 0.08$), the positions and temperature factors of the atoms of the nitrate at ($^1/_2$, 0, $^1/_2$) had refined to unrealistic values. This nitrate ion was introduced as a rigid group and was allowed to refine to a disordered position off of the inversion center; in further refinements of this nitrate with

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(12) Numbers in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digit(s).

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Table III. Positional and Thermal Parameters for $[Cu(EtaH)(Eta)]_2(NO_3)_2$

atom	*x*	*y*	*z*	B_{11} or B^a	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
				Unit A					
Cu	0.3071 (1)	−0.0077 (1)	−0.1633 (1)	2.38 (3)	2.62 (3)	2.91 (3)	1.32 (3)	0.25 (3)	1.09 (3)
O1	0.2971 (4)	−0.1593 (4)	−0.1082 (4)	2.8 (1)	2.5 (1)	3.2 (2)	1.1 (1)	0.1 (1)	1.2 (1)
C11	0.1939 (7)	−0.3065 (6)	−0.2218 (7)	3.1 (2)	2.6 (2)	4.0 (3)	1.2 (2)	−0.0 (2)	0.9 (2)
C12	0.0672 (7)	−0.3065 (6)	−0.3027 (7)	2.9 (2)	3.0 (2)	3.7 (3)	0.9 (2)	−0.3 (2)	0.7 (2)
N1	0.1454 (6)	−0.1780 (5)	−0.3418 (6)	3.0 (2)	3.8 (2)	3.2 (2)	1.6 (2)	0.0 (2)	1.0 (2)
O2	0.4699 (4)	0.1509 (4)	0.0145 (4)	3.3 (1)	2.6 (1)	3.2 (2)	1.4 (1)	0.1 (1)	1.0 (1)
C21	0.5272 (7)	0.2934 (6)	0.0149 (0)	4.0 (3)	2.5 (2)	4.8 (3)	1.4 (2)	−0.5 (2)	1.3 (2)
C22	0.3968 (8)	0.2881 (7)	−0.0650 (8)	4.2 (3)	3.1 (2)	5.2 (3)	2.1 (2)	0.4 (2)	1.6 (2)
N2	0.3240 (6)	0.1561 (5)	−0.2056 (6)	3.7 (2)	3.6 (2)	3.9 (2)	2.1 (2)	0.8 (2)	1.8 (2)
HC11A[b]	0.130 (7)	−0.382 (6)	−0.181 (7)						
HC11B	0.269 (7)	−0.324 (6)	−0.295 (6)						
HC12A	0.001 (7)	−0.278 (6)	−0.240 (7)						
HC12B	0.021 (7)	−0.393 (6)	−0.396 (7)						
HC21A	0.610 (7)	0.311 (6)	−0.057 (7)						
HC21B	0.557 (7)	0.371 (6)	0.126 (7)						
HC22A	0.454 (7)	0.384 (6)	−0.092 (6)						
HC22B	0.230 (7)	0.274 (6)	−0.029 (7)						
HN1A	0.197 (7)	−0.194 (7)	−0.411 (7)						
HN1B	0.071 (7)	−0.163 (6)	−0.371 (6)						
HN2A	0.385 (7)	0.162 (6)	−0.278 (7)						
HN2B	0.222 (7)	0.134 (6)	−0.244 (7)						
HO2	0.601 (7)	0.163 (6)	0.076 (6)						
				Unit B					
Cu	0.1563 (1)	−0.0031 (1)	0.3083 (1)	2.86 (3)	2.55 (3)	2.51 (3)	1.47 (3)	0.95 (3)	1.12 (3)
O1	0.1318 (4)	0.1547 (4)	0.4459 (4)	3.0 (1)	2.4 (1)	3.3 (2)	1.5 (1)	1.1 (1)	1.2 (1)
C11	0.2695 (7)	0.2985 (6)	0.4822 (7)	3.6 (2)	2.6 (2)	3.9 (3)	1.3 (2)	0.9 (2)	1.4 (2)
C12	0.3436 (8)	0.2920 (7)	0.3497 (8)	3.5 (2)	2.6 (2)	4.4 (3)	0.8 (2)	1.1 (2)	1.7 (2)
N1	0.3580 (6)	0.1628 (6)	0.3015 (6)	3.4 (2)	4.1 (2)	3.7 (2)	2.1 (2)	1.5 (2)	2.1 (2)
O2	−0.0433 (4)	−0.1541 (4)	0.3270 (4)	2.7 (1)	2.6 (1)	3.2 (2)	1.2 (1)	0.8 (1)	0.9 (1)
C21	−0.0741 (8)	−0.2994 (6)	0.2464 (7)	3.8 (2)	2.7 (2)	4.1 (3)	1.6 (2)	1.0 (2)	1.1 (2)
C22	0.0029 (8)	−0.3023 (7)	0.1154 (7)	5.0 (3)	3.0 (2)	3.5 (3)	2.4 (2)	0.8 (2)	0.6 (2)
N2	0.1650 (6)	−0.1729 (6)	0.1685 (6)	4.26 (2)	4.0 (2)	3.5 (2)	2.7 (2)	1.6 (2)	1.7 (2)
HC11A	0.340 (7)	0.319 (6)	0.557 (7)						
HC11B	0.247 (7)	0.381 (6)	0.512 (7)						
HC12A	0.274 (7)	0.279 (6)	0.281 (7)						
HC12B	0.421 (7)	0.358 (7)	0.372 (7)						
HC21A	−0.172 (7)	−0.366 (7)	0.217 (7)						
HC21B	−0.044 (7)	−0.324 (6)	0.307 (7)						
HC22A	−0.007 (7)	−0.392 (7)	0.064 (7)						
HC22B	−0.043 (7)	−0.295 (6)	0.058 (7)						
HN1A	0.430 (7)	0.180 (6)	0.361 (7)						
HN1B	0.390 (7)	0.148 (6)	0.221 (7)						
HN2A	0.216 (7)	−0.185 (7)	0.205 (7)						
HN2B	0.208 (7)	−0.149 (6)	0.106 (7)						
HO2	−0.095 (6)	−0.145 (6)	0.456 (7)						
HN1	0.2965 (6)	−0.3806 (6)	0.3387 (7)	3.7 (2)	4.6 (3)	5.4 (3)	2.0 (2)	1.1 (2)	2.8 (2)
ON11	0.320 (1)	−0.362 (1)	0.462 (1)	10.0 (6)	11.5 (7)	6.6 (3)	0.9 (3)	−0.6 (3)	3.6 (3)
ON12	0.202 (1)	−0.365 (1)	0.297 (2)	8.0 (6)	13.4 (7)	34 (2)	4.6 (6)	0.3 (6)	17 (1)
ON13	0.367 (2)	−0.420 (2)	0.263 (2)	22 (1)	19 (1)	17 (1)	15.3 (9)	14.5 (9)	11 (1)
NN2	0.000	0.000	0.000	3.9 (1)					
ON21	−0.021 (2)	0.009 (2)	0.125 (2)	14 (1)	10 (1)	7.6 (7)	9.2 (9)	7.7 (9)	6.3 (7)
ON22	0.983 (2)	−0.042 (2)	−0.040 (3)	10 (1)	15 (1)	14 (2)	10 (1)	10 (1)	11 (1)
ON23	−0.047 (5)	0.041 (3)	−0.058 (2)	28 (3)	18 (2)	7 (1)	19 (2)	−2 (1)	3 (1)
NN3	0.515	−0.004	0.457	9.1 (2)					
ON31	0.620	−0.010	0.500	8.4 (2)					
ON32	0.430	0.010	0.534	9.4[c]					
ON33	0.495	−0.012	0.338	6.9 (2)					

[a] The form of the thermal ellipsoid expression is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. *B* values are in Å². [b] All hydrogen atoms were assigned isotropic thermal parameters of 3.0. [c] The thermal parameter of ON32 was not refined.

isotropic temperature factors, it was still necessary to fix the temperature factor of one oxygen atom. The oxgyen atoms of the nitrate group at (0, 0, 0) were refined with anisotropic temperature factors. Hydrogen atoms were located from a difference Fourier calculation, and their positions were refined. In the final cycle of refinement, the maximum parameter shift was 0.33σ (B_{33} of NO22). Residual electron density was located largely in the vicinity of the nitrate groups. Final atomic parameters are listed in Table III. Final observed and calculated structure factors are available.

For $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$, all nonhydrogen atoms were refined anisotropically. The 23 hydrogen atoms were located as the principal features on an electron density map; in subsequent refinements, the hydrogen coordinates were varied, but the hydrogen thermal parameters were fixed at 5.0. The positional parameters of two hydrogen atoms bonded to C4 did not refine well and were fixed at calculated positions. In the final cycle of refinement, the maximum parameter shift was 0.18σ (*z* coordinate of H2C1). The major feature on a final difference Fourier map was a peak of 0.32 e Å^{-3} about 1.0 Å from Cu; this compares to values of approximately 0.40 e Å^{-3} for typical hydrogen atoms in this structure. Final atomic parameters are listed in Table IV. Final calculated and observed structure factors are available as supplementary material.

Discussion

The structure of $[Cu(EtaH)(Eta)]_2(NO_3)_2$ consists of two independent dinuclear cations, $[Cu(EtaH)(Eta)]_2^{2+}$, and three

Table IV. Positional and Thermal Parameters for $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	−0.21011 (6)	0.11258 (2)	0.07279 (2)	3.12 (1)	2.049 (8)	2.05 (1)	−0.14 (2)	0.379 (8)	−0.07 (2)
O1	−0.2514 (3)	−0.0235 (1)	0.0784 (1)	3.6 (1)	2.29 (8)	2.3 (1)	−0.00 (7)	0.32 (8)	0.00 (9)
O2	−0.3994 (4)	0.1227 (1)	−0.0403 (1)	3.7 (1)	2.4 (6)	2.5 (1)	−0.34 (7)	0.08 (8)	0.00 (9)
OW	0.1442 (5)	0.0909 (2)	0.0576 (2)	4.2 (1)	3.78 (8)	4.0 (1)	0.0 (1)	1.5 (1)	−0.74 (9)
N1	−0.0923 (5)	0.1077 (2)	0.1943 (1)	4.0 (1)	2.60 (8)	2.4 (1)	−0.3 (1)	0.79 (8)	−0.37 (9)
N2	−0.1963 (6)	0.2545 (2)	0.0647 (2)	3.4 (1)	2.44 (8)	2.7 (1)	0.0 (1)	0.79 (8)	−0.28 (9)
Cl	−0.1130 (6)	−0.0553 (2)	0.1548 (2)	4.0 (2)	2.36 (8)	2.5 (1)	0.3 (1)	0.2 (1)	0.00 (9)
C2	−0.1353 (5)	0.0111 (2)	0.2226 (2)	3.7 (1)	2.76 (8)	2.1 (1)	0.2 (1)	0.3 (1)	0.28 (9)
C3	−0.3688 (7)	0.0109 (3)	0.2316 (2)	4.9 (2)	3.9 (2)	3.8 (1)	−0.1 (2)	1.6 (2)	0.28 (9)
C4	0.0355 (7)	−0.0150 (3)	0.3021 (2)	6.0 (2)	4.3 (2)	2.7 (1)	0.3 (2)	−0.4 (2)	0.28 (9)
C5	−0.4753 (6)	0.2187 (2)	−0.0591 (2)	3.7 (1)	2.76 (8)	2.9 (1)	0.1 (1)	0.2 (1)	0.46 (9)
C6	−0.2852 (5)	0.2867 (2)	−0.0213 (2)	3.3 (1)	2.36 (8)	2.9 (1)	−0.1 (1)	0.5 (1)	0.28 (9)
C7	−0.1031 (7)	0.2797 (3)	−0.0632 (2)	4.5 (2)	4.1 (2)	3.6 (1)	−0.2 (2)	1.1 (2)	0.55 (9)
C8	−0.3764 (7)	0.3881 (3)	−0.0246 (2)	5.5 (2)	2.92 (8)	4.9 (1)	0.4 (2)	0.8 (2)	0.6 (2)
NN	0.4208 (5)	0.2635 (2)	0.1902	4.2 (1)	3.70 (8)	4.1 (1)	−0.7 (1)	1.1 (1)	−1.66 (9)
ON1	0.3529 (6)	0.2707 (2)	0.1151 (2)	7.4 (2)	8.2 (2)	3.7 (1)	−2.3 (1)	0.8 (1)	−0.83 (9)
ON2	0.2893 (6)	0.2432 (3)	0.2282 (2)	7.7 (2)	9.5 (2)	6.5 (2)	−4.6 (2)	3.9 (2)	−3.5 (2)
ON3	0.6201 (4)	0.2780 (2)	0.2232 (2)	3.8 (1)	6.4 (2)	6.6 (1)	0.2 (1)	0.4 (1)	−2.12 (9)

atom	x	y	z	atom	x	y	z
HO2	−0.514 (7)	0.088 (3)	−0.053 (2)	H1C4	0.017 (7)	0.024 (3)	0.341 (2)
H1W	0.212 (7)	0.133 (3)	0.066 (3)	H2C4	0.189	−0.004	0.294
H2W	0.170 (8)	0.072 (3)	0.025 (3)	H3C4	0.030	−0.007	0.317
H1N1	−0.140 (7)	0.152 (3)	0.222 (2)	H1C5	−0.512 (6)	0.226 (3)	−0.115 (2)
H2N1	0.042 (7)	0.120 (3)	0.203 (2)	H2C5	−0.608 (7)	0.232 (3)	−0.035 (2)
H1N2	−0.287 (7)	0.273 (3)	0.092 (2)	H1C7	−0.049 (7)	0.215 (3)	−0.064 (2)
H2N2	−0.051 (7)	0.271 (3)	0.082 (2)	H2C7	0.024 (7)	0.320 (3)	−0.036 (2)
H1C1	−0.151 (6)	−0.119 (3)	0.164 (2)	H3C7	−0.155 (7)	0.297 (3)	−0.118 (2)
H2C1	0.047 (7)	−0.057 (3)	0.154 (2)	H1C8	−0.487 (7)	0.390 (3)	0.005 (2)
H1C3	−0.388 (7)	0.052 (3)	0.268 (2)	H2C8	0.242 (7)	0.431 (3)	−0.000 (2)
H2C3	−0.465 (7)	0.026 (3)	0.182 (3)	H3C8	−0.447 (6)	0.406 (3)	−0.079 (2)
H3C3	−0.410 (7)	−0.047 (3)	0.245 (2)				

[a] The form of the thermal ellipsoid expression is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. All hydrogen atoms were assigned isotropic thermal parameters of 5.0 Å². The positional parameters of H2C4 and H3C4 were not refined.

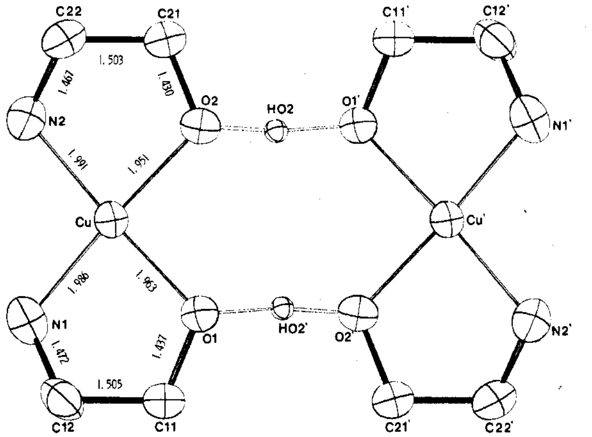


Figure 1. Structure of the dinuclear cation $[Cu(EtaH)(Eta)]_2^{2+}$ with average bond distances.

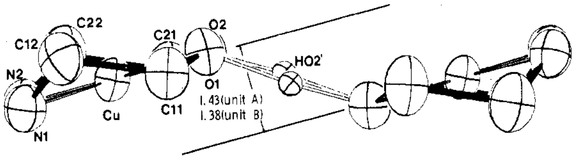


Figure 2. View of the dinuclear cation $[Cu(EtaH)(Eta)]_2^{2+}$, showing the "step" arrangement.

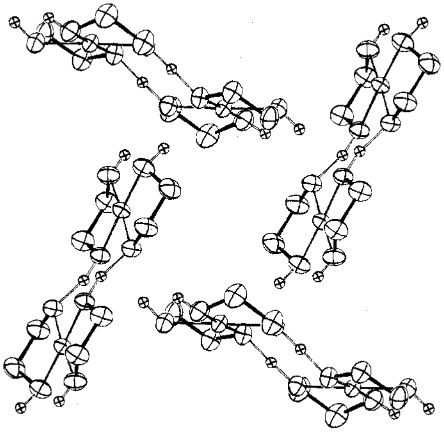


Figure 3. Packing of the dimeric cations for $[Cu(EtaH)(Eta)]_2^{2+}$.

independent nitrate ions. Although crystallographically independent, the dinuclear units are virtually identical; Figure 1 is a perspective view of the cation with the atom numbering scheme indicated. Interatomic distances and angles are presented in Table V.

Each copper(II) atom shows square-planar coordination with a cis arrangement of two 2-aminoethanol chelate ligands. None of the coordinated atoms (Table VI) is more than 0.02 Å from their least-squares plane; the copper atom shows no deviation from this plane. The copper–oxygen and copper–nitrogen distances are all in the range of 1.948–1.988 Å, and bond angles at copper range from 84.6 to 99.4°.

The bis-chelated copper(II) complexes $Cu(EtaH)(Eta)^+$ are associated into hydrogen-bonded dinuclear units about inversion centers at (${}^1/_2$, 0, 0) and (0, 0, ${}^1/_2$) with the alcohol groups serving as hydrogen-bond donors and the alkoxide oxygens serving as hydrogen-bond acceptors. The oxygen–oxygen distances of 2.452 (6) and 2.434 (6) Å are shorter than most hydrogen-bonded oxygen–oxygen distances but are considerably longer than the 2.31 Å observed for $[Cu(DiimH)]_2$. The copper–copper distances are 4.940 (5) and 4.942 (5) Å. The Cu–O1–O2′ angle and Cu′–O2′–O1 angle are 124.3 (2) and 125.1 (2)°, respectively. The two coordination planes of the dimers are parallel as a result of the center

Table V. Interatomic Distances (Å) and Angles (Deg) for $[Cu(EtaH)(Eta)]_2(NO_3)_2$

unit A		unit B	
	Distances		
Cu-Cu′	4.940 (5)	Cu-Cu′	4.942 (5)
O1-O2′	2.542 (6)	O1-O2′	2.434 (6)
Cu-O1	1.960 (4)	Cu-O1	1.966 (4)
Cu-N1	1.985 (5)	Cu-N1	1.987 (5)
Cu-O2	1.955 (5)	Cu-O2	1.948 (4)
Cu-N2	1.995 (5)	Cu-N2	1.988 (5)
O1-C11	1.442 (7)	O1-C11	1.433 (7)
C11-C12	1.501 (8)	C11-C12	1.509 (9)
C12-N1	1.481 (8)	C12-N1	1.463 (8)
O2-C21	1.433 (7)	O2-C21	1.427 (7)
C21-C22	1.490 (9)	C21-C22	1.517 (9)
C22-N2	1.470 (9)	C22-N2	1.464 (9)
C11-HC11A	1.02 (6)	C11-HC11A	0.91 (6)
C11-HC11B	1.08 (6)	C11-HC11B	0.96 (6)
C12-HC12A	1.00 (6)	C12-HC12A	0.89 (6)
C12-HC12B	0.97 (6)	C12-HC12B	0.71 (6)
C21-HC21A	1.09 (6)	C21-HC21A	0.85 (6)
C21-HC21B	1.06 (6)	C21-HC21B	0.86 (6)
C22-HC22A	1.09 (6)	C22-HC22A	0.92 (6)
C22-HC22B	0.81 (6)	C22-HC22B	0.78 (6)
N1-HN1A	0.88 (6)	N1-HN1A	0.83 (6)
N1-HN1B	0.91 (6)	N1-HN1B	0.86 (6)
N2-HN2A	0.94 (6)	N2-HN2A	0.72 (6)
N2-HN2B	0.96 (6)	N2-HN2B	0.81 (6)
O2-HO2	1.37 (6)	O2-HO2	1.38 (6)
NN1-ON11	1.18 (1)	NN2-ON21	1.25 (1)
NN1-ON12	1.15 (1)	NN2-ON22	1.20 (2)
NN1-ON13	1.16 (1)	NN2-ON23	1.18 (2)
	Angles		
O1-Cu-N1	84.9 (2)	O1-Cu-N1	84.6 (2)
N1-Cu-N2	98.6 (2)	N1-Cu-N2	99.4 (2)
O1-Cu-O2	91.4 (2)	O1-Cu-O2	91.1 (2)
N2-Cu-O2	85.0 (2)	N2-Cu-O2	84.9 (2)
Cu-O1-C11	111.9 (3)	Cu-O1-C11	112.0 (3)
O1-C11-C12	108.0 (5)	O1-C11-C12	107.5 (5)
C11-C12-N1	107.9 (5)	C11-C12-N1	108.1 (5)
C12-N1-Cu	106.2 (4)	C12-N1-Cu	106.9 (4)
Cu-O2-C21	111.2 (3)	Cu-O2-C21	111.9 (3)
O2-C21-C22	109.2 (5)	O2-C21-C22	109.1 (5)
C21-C22-N2	108.0 (5)	C21-C22-N2	107.5 (5)
C22-N2-Cu	106.7 (4)	C22-N2-Cu	107.1 (4)
O2-HO2-O1′	172 (6)	O2-HO2-O1′	170 (6)
O1N1-NN1-O2N1	119 (1)	O1N2-NN2-O2N2	116 (1)
O2N1-NN1-O3N1	123 (1)	O2N2-NN2-O3N2	134 (1)
O1N1-NN1-O3N1	117 (1)	O1N2-NN2-O3N2	105 (1)

Table VI. Least-Squares Planes within the Molecule $[Cu(EtaH)(Eta)]_2(NO_3)_2$[a,b]

atom	dev, Å	atom	dev, Å
Equation: $0.839x + 0.243y - 0.487z - 3.479 = 0$[c]			
O1	−0.021	N2	−0.020
O2	0.021	Cu	0.000
N1	0.020	Cu′	1.425
Equation: $0.560x - 0.325y + 0.762z - 3.437 = 0$[d]			
O1	−0.011	N2	−0.011
O2	0.011	Cu	0.004
N1	0.011	Cu′	1.380

[a] Direction cosines of the planes refer to the orthogonal axis system *a, b, c**. [b] All atoms weighted at unity. [c] Plane involving four atoms (O1, O2, N1, and N2) coordinated to Cu (unit A). [d] Plane involving four atoms (O1, O2, N1, and N2) coordinated to Cu (unit B).

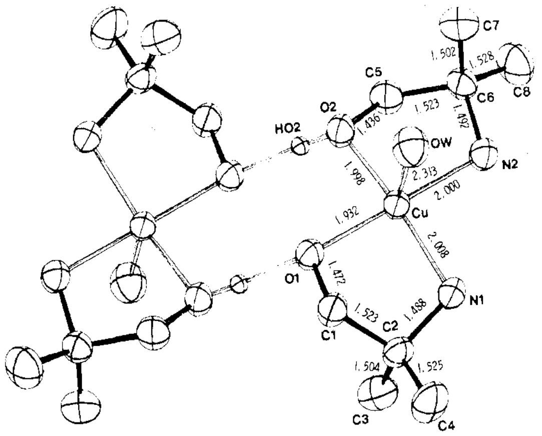


Figure 4. Structure of the dinuclear cation $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$ with bond distances.

Table VII. Interatomic Distances (Å) and Angles (Deg) for $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$[a]

	Distances		
Cu-Cu′	5.156 (1)	O2-HO2	0.85 (4)
Cu-Cu″	4.934 (1)	O1″-HO2	1.67 (4)
O2-O1″	2.516 (3)	N1-H1N1	0.89 (4)
Cu-O1	1.932 (2)	N1-H2N1	0.83 (4)
Cu-O2	1.978 (2)	N2-H1N2	0.86 (4)
Cu-N1	2.008 (3)	N2-H2N2	0.90 (4)
Cu-N2	2.000 (3)	C1-H1C1	0.95 (4)
Cu-OW	2.313 (5)	C1-H2C1	1.00 (4)
O1-C1	1.472 (3)	C3-H1C3	0.86 (4)
C1-C2	1.523 (4)	C3-H2C3	0.91 (4)
C2-N1	1.488 (4)	C3-H3C3	0.90 (4)
C2-C3	1.504 (5)	C4-H1C4	0.89 (4)
C2-C4	1.525 (4)	C4-H2C4	1.02
O2-C5	1.436 (4)	C4-H3C4	0.91
C5-C6	1.523 (4)	C5-H1C5	0.93 (4)
C6-N2	1.492 (4)	C5-H2C5	1.03 (4)
C6-C7	1.502 (4)	C7-H1C7	0.97 (4)
C6-C8	1.528 (5)	C7-H2C7	0.98 (4)
NN-ON1	1.242 (4)	C7-H3C7	0.94 (4)
NN-ON2	1.210 (4)	C8-H1C8	0.96 (5)
NN-ON3	1.234 (4)	C8-H2C8	1.02 (4)
		C8-H3C8	0.94 (4)
	Angles		
O1-Cu-N1	86.0 (1)	C4-C2-N1	111.4 (2)
N1-Cu-N2	95.5 (1)	Cu-O2-C5	111.0 (2)
O1-Cu-O2	93.9 (1)	O2-C5-C6	108.8 (2)
N2-Cu-O2	83.5 (1)	C5-C6-C7	110.9 (3)
OW-Cu-O1	91.1 (1)	C5-C6-C8	109.3 (3)
OW-Cu-O2	103.5 (1)	C6-N2-Cu	111.1 (2)
OW-Cu-N1	91.2 (1)	C7-C6-N2	108.9 (3)
OW-Cu-N2	93.6 (1)	C8-C6-N2	110.7 (3)
Cu-O1-C1	107.4 (1)	ON1-NN-ON2	119.0 (3)
O1-C1-C2	111.3 (2)	ON2-NN-ON3	122.6 (3)
C1-C2-C3	111.6 (3)	ON1-NN-ON3	118.5 (4)
C1-C2-C4	110.2 (3)	O2-HO2-O1″	177 (4)
C2-N1-Cu	108.7 (1)	Cu-O2-O1″	117.2 (1)
C3-C2-N1	107.4 (3)	O2-O1″-Cu″	130.6 (1)

[a] X and X′ are related by the inversion operation. X and X″ are related by inversion, translation operation.

of inversion (Figure 2). The two parallel coordination planes of the two independent dimers are separated by 1.43 and 1.38 Å.

Th dimeric units pack together in the solid (Figure 3) with two amine nitrogens of one dimeric unit approaching an alkoxide oxygen and an alcohol oxygen of another dimeric unit. This approach, with nitrogen–oxygen distances ranging from 3.043 (7) to 3.124 (7) Å, indicates a weak hydrogen-bonding network in this structure.

The structure of the copper complex of 2-amino-2-methylpropanol is best represented by the formula $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$, and the structure of the cation resembles that of $[Cu(EtaH)(Eta)]_2^{2+}$. Figure 4 is a perspective view of the cation with the atom numbering scheme indicated. Interatomic distances and angles are presneted in Table VII.

The coordination of the copper is a distorted tetragonal pyramid with a water molecule in the axial position. The

Table VIII. Least-Squares Plane[a, b] for $[Cu(MepH)(Mep)(H_2O)]_2(NO_3)_2$

atom	dev, Å	atom	dev, Å
Equation: $-0.971x + 0.114y + 0.212z - 2.199 = 0$[c]			
O1	−0.089	N2	−0.087
O2	0.090	Cu	−0.166
N1	0.086	Cu′	1.816

[a] Direction cosines of the plane refer to the orthogonal axis system *a*, *b*, *c**. [b] Derived by using unit weights for all atoms marked without asterisks and zero weights for atoms marked with asterisks. [c] The plane of the four atoms strongly coordinated to copper.

Table IX. Observed and Calculated Magnetic Susceptibilities (10^{-3} cgsu) for the Dimeric Compounds

	$[Cu(EtaH)(Eta)]_2$-$(NO_3)_2$		$[Cu(MepH)(Mep)(H_2O)]_2$-$(NO_3)_2$	
temp, K	obsd	calcd[a]	obsd	calcd[b]
298	2.628	2.663	2.831	2.814
293	2.710	2.704	2.863	2.856
283	2.812	2.789	2.928	2.942
273	2.884	2.880	3.049	3.034
263	2.968	2.977	3.129	3.132
253	3.078	3.081	3.258	3.236
243	3.184	3.192	3.350	3.347
233	3.332	3.312	3.438	3.467
223	3.458	3.441	3.564	3.595
213	3.550	3.580	3.711	3.732
203	3.738	3.731	3.872	3.800
193	3.878	3.894	4.038	4.040
183	4.116	4.073	4.222	4.213
173	4.264	4.267	4.384	4.400
163	4.468	4.481	4.652	4.604
153	4.736	4.715	4.844	4.824
143	4.970	4.974	5.090	5.064
133	5.250	5.260	5.317	5.324
123	5.548	5.576	5.569	5.605
113	5.992	5.926	5.860	5.906
103	6.234	6.313	6.290	6.224
93	6.746	6.736	6.531	6.550

[a] $2J = -56$ cm^{-1}, $g = 2.11$, $N\alpha = 59 \times 10^{-6}$. [b] $2J = -70$ cm^{-1}, $g = 2.18$, $N\alpha = 99 \times 10^{-6}$.

position of the copper atom is 0.17 Å above the plane (Table VIII) formed by the four coordinated atoms of the chelate ligands. The axial copper–oxygen distance (2.313 (5) Å) is considerably longer than the copper–oxygen distances in the basal plane (1.932 (2) and 1.978 (2) Å).

The bis-chelate complexes $Cu(MepH)(Mep)(H_2O)^+$ are associated into a hydrogen-bonded dinuclear unit about an inversion center at ($-{}^1/_2$, 0, 0). The oxygen–oxygen distance of 2.516 (3) Å is longer than the oxygen–oxygen distances of 2.452 (6) and 2.434 (6) Å for $[Cu(EtaH)(Eta)]_2^{2+}$. However, the copper–copper distance of 4.934 (1) Å is slightly shorter. In this compound the eight-membered ring is slightly distorted with the Cu–O2–O1″ and Cu–O1–O2″ angles (where X and X″ are related by the center of inversion at ($-{}^1/_2$, 0, 0) of 117.2 (1) and 130.6 (1)°, respectively. The two basal coordination planes are separated by a distance of 1.65 Å (Figure 5).

There is additional hydrogen bonding connecting the two copper complexes related by the inversion center at (0, 0, 0). The hydrogen bonding involves one of the water protons and O1′ and forms another eight-membered ring. The oxygen–oxygen distance of 2.756 Å and the copper–copper distance of 5.156 Å are indicative of weaker but significant hydrogen bonding. As a result of the hydrogen bonding into dimers (O1–H–O2) and between dimers (OW–H–O1′), the complexes are connected into infinite chains parallel to the *a* axis.

The nitrate anion appears to be associated with two amino groups by weak hydrgen bonds; N1–ON2 and N2–ON1 distances are 2.977 (5) and 3.302 (7) Å, respectively. N1′–H2N1–ON2 and N2–H2N2–ON1 angles are 142 (4) and 164 (3)°, respectively.

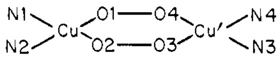
In order to explore the relationship between structural parameters and magnetic properties, the magnetic susceptibilities of these compounds were measured from 93 K to room temperature. For the nitrogen–oxygen hydrogen-bonded trinuclear complex with *l*-ephedrine, $[Cu(Eph)_2]_3 \cdot 2C_6H_6$, the magnetic moment per gram-atom of copper (Table I) was constant over the temperature range studied. The apparent absence of spin exchange may be related to the weak hydrogen bonding (N–O = 2.87 Å), or it may be related to the angle between the coordination planes of the copper ions.

The magnetic moments of the oxygen–oxygen hydrogen-bonded dinuclear complexes (Table I) decreased as the temperature was lowered, indicating antiferromagnetic coupling. Least-squares methods were used to fit the measured susceptibilities to the Bleaney and Bowers equation,[17] and the

Table X. Some Magnetic and Structural Parameters for Hydrogen-Bonded Dimers

	$[Cu(EtaH)(Eta)]_2^{2+}$		$[Cu(MepH)(Mep)$-$(H_2O)]_2^{2+}$	$[CuDiimH]_2$	
	A	B		A	B
$2J$, cm^{-1}	−56		−70	−94	
g	2.11		2.18	2.04	
$N\alpha$, 10^{-6} cgsu	59		99	118	
Cu–Cu′, Å	4.940	4.942	4.934	4.989	4.987
O1–O4, Å	2.452	2.434	2.516	2.33	2.31
O2–O3, Å	2.452	2.434	2.516	2.33	2.31
av Cu–O, Å	1.958	1.957	1.955	1.947	1.947
av Cu–N, Å	1.990	1.988	2.004	1.898	1.912
separation of two planes, Å	1.43	1.38	1.65	0.46	0.22
distance of Cu from its coordination plane, Å	0.001	0.004	0.169		
O1–Cu–O2, deg	91.4	91.1	93.9	93.1	92.8
O4–Cu′–O3, deg	91.4	91.1	93.9	93.1	92.8
Cu–O1–O4, deg	124.3	123.5	130.6	133.3	134.6
O1–O4–Cu′, deg	125.1	126.8	117.2	131.6	132.1
Cu–O2–O3, deg	125.1	126.8	117.2	131.6	132.1
O2–O3–Cu′, deg	124.3	123.5	130.6	133.3	134.6

[a] Numbering scheme of atoms is



X*n* and X(*n* + 2) (where X is oxygen or nitrogen atom and *n* is 1 or 2) are related by an inversion center for Cu(Eta), Cu(Mep), and Cu(DiimH).

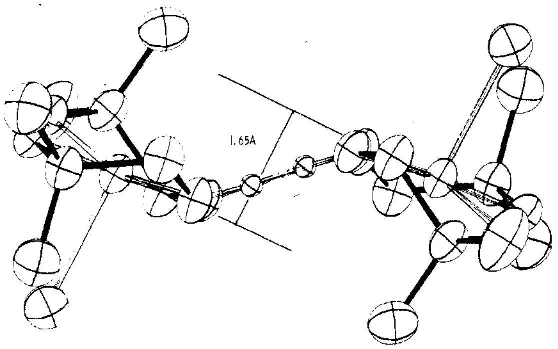


Figure 5. View of the dinuclear cation $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$, showing the "step" arrangement.

results are presented in Table IX.

The hydrogen-bonded complexes $[Cu(EtaH)(Eta)]_2^{2+}$, $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$, and $[Cu(DiimH)]_2$ have very similar structures although in $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$ the coordination of copper is square pyramidal and the other compounds exhibit square-planar coordination. Magnetic and structure parameters are listed in Table X. The two coordination planes (*xy* planes of copper atoms) of each dimer are parallel as a result of a center of inversion, but the separation of these two planes varies from 0.22 Å in one of the $[Cu(DiimH)]_2$ units to 1.65 Å in $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$. The hydrogen-bonded O–O distances also show considerable variation from the 2.31 Å of $[Cu(DiimH)]_2$ to the 2.52 Å of $[Cu(MepH)(Mep)(H_2O)]_2^{2+}$.

Although the strongest antiferromagnetic coupling corresponds to the shortest hydrogen-bonded oxygen–oxygen distance, there is no direct correlation between these parameters for the three compounds; no correlation of the coupling constants with the copper–copper distances or the separation of the coordination planes is apparent for the series of compounds. It is probable that a number of factors, including coordination geometry of copper and additional weak hydrogen bonds, affect the magnitude of the coupling and additional examples of this type of structure are needed for an understanding of these factors.

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Registry No. $[Cu(EtaH)(Eta)]_2(NO_3)_2$, 73522-88-0; $[Cu(MepH)(Mep)]_2(NO_3)_2 \cdot 2H_2O$, 73496-14-7; $[Cu(Eph)_2]_3$, 73522-29-9.

Supplementary Material Available: A listing of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectral Characterization, and Molecular Structure of [*N*-(2-Pyridylmethyl)-L-aspartato](L-phenylalaninato)cobalt(III) Trihydrate, [Co(PLASP)(L-Phe)]·3H₂O

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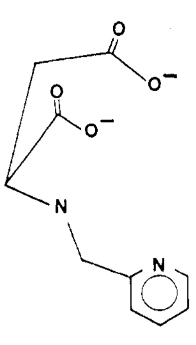
The new $Co^{III}N_3O_3$ complex $[Co(PLASP)(L\text{-}Phe)] \cdot 3H_2O$ was prepared by the oxidation of Co(II) to Co(III) in the presence of *N*-(2-pyridylmethyl)-L-aspartic acid, $PLASPH_2$, and L-phenylalanine, L-Phe. The crystal and molecular structure of the complex, determined by three-dimensional X-ray analysis, established that of the four possible geometrical isomers, the only isomer isolated was a facial isomer in which the β-COO⁻ and the pyridine groups of $PLASP^{2-}$ are mutually trans. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 9.821$ (3) Å, $b = 23.069$ (4) Å, $c = 9.564$ (2) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a final R factor of 0.059. The geometry around the cobalt atom is distorted octahedral, with the $PLASP^{2-}$ ligand being tetradentate and the L-phenylalaninate ligand bidentate. In addition to the crystal structure, the ^1H NMR and visible spectra of $[Co(PLASP)\ (L\text{-}Phe)] \cdot 3H_2O$ are discussed.

Introduction

Studies in this laboratory have shown that metal complexes of certain asymmetric tetradentate ligands exhibit stereoselective effects in coordinating optically active amino acids.[1,2] In order to better understand these effects, we have synthesized a series of mixed complexes of the type Co(PLASP)(AA), where $PLASP^{2-}$ is the dianion of the tetradentate *N*-(2-pyridylmethyl)-L-aspartic acid ligand and AA⁻ is the anion of one of the following amino acids: D- or L-phenylalanine, D-, DL-, or L-valine, L-alanine, L-threonine, L-proline, glycine, and α-aminoisobutyric acid.[3] Although there are four possible geometrical isomers (Figure 1) of these complexes, only one was isolated for all the amino acids listed above. The visible spectra of these complexes, when compared to the spectra of various $Co^{III}N_3O_3$ complexes reported in the literature support a facial arrangement of the oxygen (or nitrogen) atoms around



$PLASP^{2-}$

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