the observed formate derivative (eq 8). Both of these reactions

$$[ReH(diphos)_2] + CO_2 \rightleftarrows [ReH(CO_2)(diphos)_2] \quad (7)$$

$$[ReH(CO)_2(diphos)_2] \rightleftarrows [Re(O_2CH)(diphos)_2] \quad (8)$$

must be reversible, however, since CO_2 is readily displaced by N_2 and H_2 to yield $[ReH(N_2)(diphos)_2]$ and $[ReH_3(diphos)_2]$, respectively, and CO_2 is liberated upon thermal decomposition of $[Re(O_2CH)(diphos)_2]$. Reactivity studies of this complex directed toward further reduction or release of the coordinated HCO_2^- ligand and attempts to prepare other adduct complexes are currently underway in these laboratories.

Acknowledgment. We are indebted to Dr. A. P. Ginsberg of Bell Laboratories for the generous gifts of $[ReH_3(diphos)_2]$ and $[ReH(N_2)(diphos)_2]$. We thank Alan Freyer and Dr. Robert Minard for assistance in obtaining NMR and mass spectra, respectively, and the National Science Foundation for support of this research. The JEOL PS-100-FT NMR spectrometer and the AEI-MS-902 mass spectrometer used in this research were purchased with the aid of grants from the National Science Foundation's major equipment grant program. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award and the Alfred P. Sloan Foundation for a research fellowship.

Magnetic Exchange Interactions in Binuclear Copper(II) Complexes with Only a Single Hydroxo Bridge: The X-ray Structure of μ-Hydroxo-tetrakis(2,2′-bipyridine)dicopper(II) Perchlorate

Muin S. Haddad,[1] Scott R. Wilson,[2] Derek J. Hodgson,*[2] and David N. Hendrickson*[1]

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. *Received June 16, 1980*

Abstract: The X-ray structure of $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$, where bpy is 2,2′-bipyridine, has been determined on an automatic Picker four-circle diffractometer, by use of 4528 ($F_o > 3\sigma$) unique reflections, to give final discrepancy indices of $R_1 = 0.069$ and $R_2 = 0.087$. The complex crystallizes in the monoclinic space group $P2_1/n$ in a cell having the dimensions of $a = 14.839$ (8) Å, $b = 18.197$ (9) Å, $c = 16.491$ (8) Å, and $\beta = 92.87$ (3)°. The observed and calculated densities are 1.61 (2) and 1.594 g cm^{-3}, respectively. The complex is comprised of perchlorate counterions and binuclear $[(bpy)_2Cu-OH-Cu(bpy)_2]^{3+}$ cations. The two copper(II) ions in the binuclear unit are bridged by only a single hydroxide ion with an Cu-O-Cu bridging angle of 141.6 (3)°. No crystallographic symmetry is imposed on the binuclear units. The coordination geometry about each copper ion is approximately trigonal bipyramidal with the bridging hydroxide ion occupying an equatorial site. The distortion from trigonal-bipyramidal coordination geometry is greater for one of the copper ions in the binuclear cation by virtue of one perchlorate oxygen atom approaching the copper ion in a sixth site to give an Cu-O distance of 3.047 (9) Å. Magnetic susceptibility data were collected from 286 to 4.2 K for $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ and the analogous compound $[(phen)_2Cu-OH-Cu(phen)_2](ClO_4)_3$, where phen is 1,10-phenanthroline. Relatively strong antiferromagnetic exchange interactions are present in both complexes, as evidenced by the 286 K effective magnetic moments of 1.56 and 1.35 μ_B, respectively. The data were least-squares fit to the theoretical susceptibility equation resultant from the spin Hamiltonian $\mathbf{H} = -2J\hat{S}_1\cdot\hat{S}_2$ to give $J = -161$ cm^{-1} for the bpy complex and $J = -177$ cm^{-1} for the phen complex.

Introduction

A linear relationship has been noted[3-6] between the bridge angle, Cu-O-Cu, and the magnetic exchange parameter J (i.e., parameter in the spin Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$) for a series of some 11 binuclear dihydroxo-bridged copper(II) complexes. Kahn, Jeannin, and co-workers[7] reported that the compound di-μ-hydroxo-tetrakis(cyclohexylamine)dicopper(II) perchlorate does not fit into the linear relationship. This compound is different from all other dihydroxo-bridged systems in that the coordination planes about the two copper(II) ions are not coplanar but are bent at a dihedral angle of 147.5°. Hydroxo-bridged binuclear copper(II) complexes have very recently been found[8] to be catalytically active for oxidative coupling reactions, a fact that adds to the practical importance of studying the electronic structure of such complexes.

Until recently, no examples of binuclear copper(II) complexes bridged by *only* a single hydroxide ion were known. The preparation and physical properties of $[(tren)Cu-OH-Cu(tren)]X_3$, where tren is tris(2-aminoethyl)amine and X is PF_6^- or ClO_4^-, have been reported.[9] As far as we know, these are the only reported examples of binuclear copper(II) complexes bridged by only one hydroxide ion. Strong antiferromagnetic exchange interactions characterized by J values of −350 (PF_6^-) and −360 cm^{-1} (ClO_4^-) were noted.

In this paper are reported the preparation and characterization of two new binuclear copper(II) complexes bridged by only a single hydroxide ion, $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ and $[(phen)_2Cu-OH-Cu(phen)_2](ClO_4)_3$. Magnetic susceptibility data are presented and, consequently, it was important to determine the structure of at least one of these two complexes. The results of an X-ray structure of the bpy complex are given.

In addition to examining further the relationship between Cu-O-Cu angle and exchange parameter, binuclear copper(II) complexes with one hydroxide bridge could prove useful in es-

(1) University of Illinois.
(2) University of North Carolina.
(3) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.
(4) Ivarsson, G. J. M. *Acta Chem. Scand., Ser. A* **1979**, *33A*, 323.
(5) Arcus, C.; Fivizzani, K. P.; Pavkovic, S. F. *J. Inorg. Nucl. Chem.* **1977**, *39*, 285.
(6) Näsäkkälä, M. *Ann. Acad. Sci. Fenn, Ser. A2* **1977**, 181.
(7) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Abaul, J.; Martin-Frere, J. *Inorg. Chem.* **1979**, *18*, 1675.
(8) Meinders, H. C.; Van Bolhuis, F.; Challa, G. *J. Mol. Catal.* **1979**, *5*, 225.
(9) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chim. Acta* **1978**, L121.

0002-7863/81/1503-384$01.00/0

tablishing the nature of the Fe(III)–Cu(II) interaction present for the heme a_3–copper(II) association in cytochrome oxidase. Apparently, there is an antiferromagnetic exchange interaction[10] with $-J \geq 200$ cm^{-1}, which has been attributed to an interaction between a heme high-spin ferric ion and a copper(II) ion as propagated by an imidazolate anion.[11] The imidazolate bridge model has been attacked.[12-14] On the other hand, the preliminary work[9] on binuclear copper(II) complexes bridged by a single hydroxide ion points to the possibility that the Fe(III)–Cu(II) bridge in cytochrome oxidase is a hydroxide ion or some other single atom bridge.

Experimental Section

Compound Preparation. The compound $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ was prepared in the following manner. To a 50-mL aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.50 g) was added 0.88 g of 2,2′-bipyridine. Ethyl alcohol (ca. 5 mL) was added, and the resulting solution was then stirred until most of the bpy dissolved. To the filtered blue solution was added 0.1 mL of $(Et)_3N$. The solution turned blue-green. A solution of $NaClO_4$ (0.36 g in 7 mL of H_2O) was added slowly. The solution was continually stirred, and after all of the $NaClO_4$ solution was added, the product separated. The blue-green fine crystalline material was collected, washed with ether, and dried in vacuo over P_4O_{10}. Crystals were obtained by dissolving approximately 0.40 g of the compound in 60 mL of hot water and subsequent slow cooling of the solution. Blue crystals were formed. Among the bulk of the crystals a few well-formed crystals of the compound $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ were formed. The other crystals were of a much brighter color. Anal. Calcd for $C_{40}H_{33}N_8O_{13}Cu_2Cl_3$: C, 45.03; H, 3.09; N, 10.50; Cu, 11.91. Found: C, 45.03; H, 2.98; N, 10.22; Cu, 11.79.

A sample of the compound $[(phen)_2Cu-OH-Cu(phen)_2](ClO_4)_3$ was prepared by the following procedure. To a solution of $CuSO_4{\cdot}5H_2O$ (0.50 g in 40 mL of ethanol and 60 mL of H_2O) was added 0.74 g of 1,10-phenanthroline. While the solution was continually stirred, the blue color intensified and at the same time a fine precipitate formed. To this mixture was added 0.06 g of KOH, and the solution was then filtered. An aqueous solution of $NaClO_4$ (ca. 2.0 g) was added to the filtrate. Almost instantaneously a blue-green product precipitated. The product was recrystallized from hot water. Anal. Calcd for $C_{48}H_{33}N_8Cu_2Cl_3O_{13}$: C, 49.57; H, 2.84; N, 9.57; Cu, 10.92. Found: C, 49.48; H, 2.76; N, 9.59; Cu, 10.77.

Physical Measurements. Variable-temperature (4.2–286 K) magnetic susceptibility data were obtained with a Princeton Applied Research Model 150A vibrating-sample magnetometer operating at 13.5 kG and calibrated with $CuSO_4{\cdot}5H_2O$ as described in a previous paper.[15] All data were corrected for diamagnetism[16] and TIP (taken as 120×10^{-6} cgsu/mol of binuclear complex). All least-squares fittings of susceptibility data to theoretical equations were performed by using a new version of the minimization computer program STEPT.[17]

EPR spectra of powdered samples were recorded on a Varian E-9 X-band spectrometer and a Varian E-15 Q-band spectrometer as described previously.[18] Infrared spectra were measured with a Perkin-Elmer Model 467 spectrophotometer. Samples were prepared as 13-mm KBr pellets.

Collection and Reduction of the X-ray Data. On the basis of precession and Weissenberg photography the deep blue prismatic crystals were assigned to the monoclinic system. The observed systematic absences of $0k0$ for k odd and $h0l$ for $(h + l)$ odd are consistent only with the centrosymmetric space group $P2_1/n$, which is a nonstandard setting of the conventional space group $P2_1/c$ (C_{2h}^5). The cell constants, obtained by least-squares procedures,[19] are a = 14.839 (8), b = 18.197 (9), c = 16.491 (8) Å, and β = 92.87 (3)°. A density of 1.594 g cm^{-3} calculated for four formula units in the cell is in acceptable agreement with that of 1.61 (2) g cm^{-3} observed by flotation in carbon tetrachloride/bromoform mixtures. Thus, in space group $P2_1/n$, no crystallographic symmetry is imposed on the dinuclear units.

An irregularly shaped crystal bounded by faces of the forms {011} and by the faces (111), $(\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(11\bar{1})$, $(\bar{1}1\bar{1})$, and $(1\bar{1}1)$ was chosen for data collection. The separations between opposite faces were as follows: (011) to $(0\bar{1}\bar{1})$, 0.475 mm; $(01\bar{1})$ to $(0\bar{1}1)$, 0.542 mm; (111) to $(\bar{1}\bar{1}\bar{1})$, 0.381 mm; $(\bar{1}\bar{1}1)$ to $(11\bar{1})$, 0.784 mm; $(\bar{1}1\bar{1})$ to $(1\bar{1}1)$, 0.477 mm. Intensity data were collected with the crystal mounted on a glass fiber roughly parallel to the (011) face.

The data were collected on an automatic Picker four-circle diffractometer equipped with Mo Kα radiation and a graphite monochromator at a takeoff angle of 1.5°; the counter aperture was 5.0 × 5.0 mm and was placed 32 cm from the crystal. Data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min, the peaks being scanned from 0.80° in 2θ below the calculated Kα_1 peak position to 0.80° in 2θ above the calculated Kα_2 peak position. Stationary counter, stationary crystal backgrounds of a 20-s duration were recorded at both ends of each scan.

A unique data set having 2θ (Mo Kα_1) $\leq 50°$ was collected; there were extremely few observable reflections at $2\theta > 50°$. After every 100 reflections, the intensities of three standard reflections were monitored; these standards showed no significant change in intensity during the data collection period. The total number of data recorded (including space group extinct data and standards) was 8378. Data processing was carried out in the manner described elsewhere.[20,21] The intensities and their estimated standard deviations were corrected for Lorentz–polarization effects and for absorption. The absorption coefficient for these atoms and Mo Kα radiation is 12.10 cm^{-1} and for the sample chosen the transmission coefficients ranged from 0.59 to 0.72 with an average value of 0.66. Of the data gathered, only 4528 were independent data whose intensities exceeded 3 times their estimated standard deviations; only these data were used in the subsequent structure analysis.

Solution and Refinement of the Structure. The positions of the two independent copper atoms were deduced from a three-dimensional Patterson function.[22] The locations of the remaining nonhydrogen atoms were determined from subsequent difference Fourier maps and were refined by least-squares methods. All least-squares calculations were on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were assigned as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for nonhydrogen atoms were taken from ref 23a, while those for hydrogen were from the tabulation of Stewart, Davidson, and Simpson.[24] The effect of the anomalous dispersion of Cu and Cl was included in the calculations, the values of $\Delta f'$ and $\Delta f''$ being from ref 23b.

Isotropic refinement of all nonhydrogen atoms gave values of the residuals $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$ of 0.142 and 0.188, respectively. The hydrogen atom of the bridging hydroxyl group was located in a difference Fourier map, while the bipyridine hydrogen atom locations were calculated on the basis of C–H distances of 0.95 Å[25] and trigonal geometry at carbon. In the final cycles of least-squares refinement, the hydrogen atoms were assigned fixed isotropic thermal parameters of 1.5 Å^2 greater than those of the carbon (or oxygen) atom to which they were attached, and no hydrogen parameter was varied. The final least-squares calculation involved anisotropic refinement of all Cu, Cl, O, and N atoms and isotropic refinements of the carbon atoms; this leads to 395 variables for the 4528 observations. The final values of the agreement factors R_1 and R_2 were 0.069 and 0.087, respectively. No atomic parameter exhibited a shift greater than 0.6 σ, which was taken as evidence that the refinement had converged. Examination of the final values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was required, and none was applied. The value of R_2 showed no unexpected trends as a function of sin θ or of $|F_o|$, which suggests that our weighting scheme is appropriate.

It is apparent that two to the three perchlorate groups are undergoing considerable thermal motion and may indeed be disordered. Examination of Fourier maps throughout the course of the analysis did not reveal any meaningful disordered model, however, and the best description of these

(10) Tweedle, M. F.; Wilson, L. J.; Garcia-Iniguez, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, *253*, 8065.

(11) Palmer, G.; Babcock, G. T.; Vickery, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2206.

(12) Landrum, J. T.; Reed, C. A.; Hatano, K.; Scheidt, W. *J. Am. Chem. Soc.* **1978**, *100*, 3232.

(13) Haddad, M. S.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 2622. Haddad, M. S.; Duesler, E. N.; Hendrickson, D. N. *Ibid.* **1979**, *18*, 141.

(14) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 265 and references therein.

(15) Hasty, E. F.; Wilson, L.; Hendrickson, D. N. *Inorg. Chem.* **1978**, *17*, 1834.

(16) Selwood, P. W. "Magnetochemistry", 2nd ed.; Interscience: New York, 1956; pp 78, 92, 93.

(17) Chandler, J. P., Program 66, Quantum Chemistry Program Exchange; Indiana University: Bloomington, Indiana, 1973.

(18) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077.

(19) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

(20) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(21) Purnell, L. G.; Shepherd, J. C.; Hodgson, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2376.

(22) For a description of the programs used, see: Estes, E. D.; Hodgson, D. J. *Inorg. Chem.* **1973**, *12*, 2932.

(23) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2A; (b) Table 2.3.1.

(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

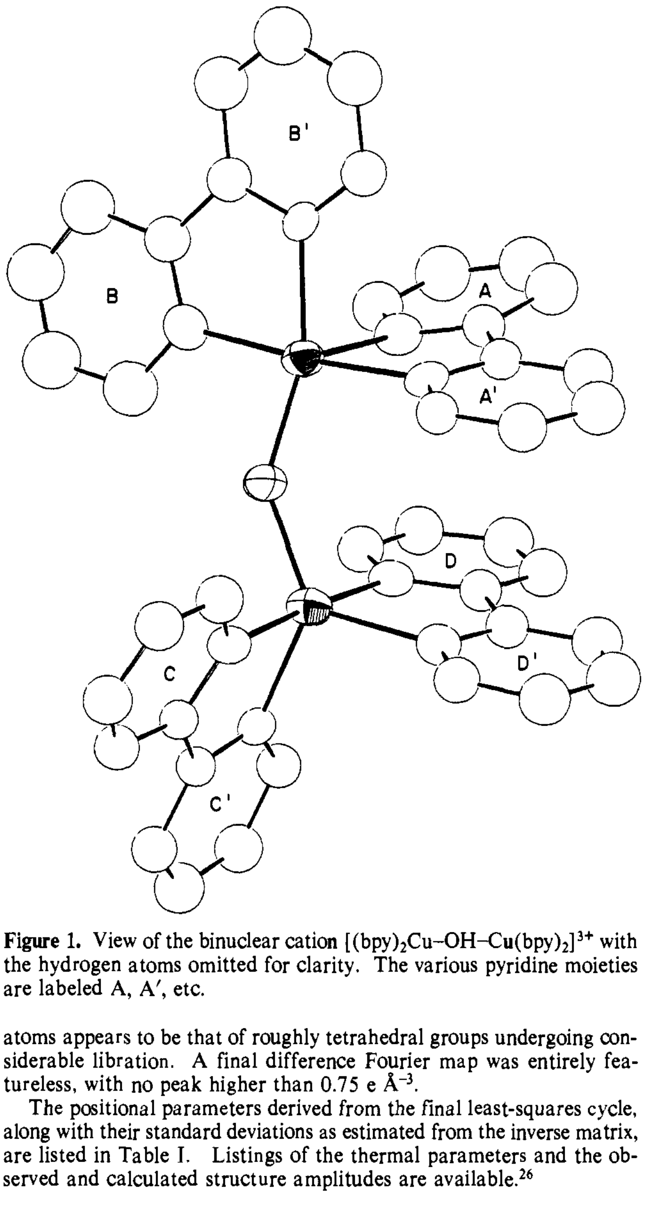


Figure 1. View of the binuclear cation $[(bpy)_2Cu-OH-Cu(bpy)_2]^{3+}$ with the hydrogen atoms omitted for clarity. The various pyridine moieties are labeled A, A', etc.

atoms appears to be that of roughly tetrahedral groups undergoing considerable libration. A final difference Fourier map was entirely featureless, with no peak higher than 0.75 e Å^{-3}.

The positional parameters derived from the final least-squares cycle, along with their standard deviations as estimated from the inverse matrix, are listed in Table I. Listings of the thermal parameters and the observed and calculated structure amplitudes are available.[26]

Results and Discussion

Description of the Structure. The structure consists of binuclear $[(bpy)_2Cu-OH-Cu(bpy)_2]^{3+}$ cations which are moderately well separated from the perchlorate anions. The geometry of the binuclear cation is shown in Figure 1, and the inner coordination spheres around the two copper(II) centers are depicted in Figure 2. The complex consists of two approximately trigonal-bipyramidal copper(II) centers, wherein the bridging oxygen atom occupies an equatorial site on each copper atom while the remaining sites are filled by the nitrogen atoms of the bipyridine ligands. The distortion from trigonal-bipyramidal geometry is much less severe for Cu(2) than for Cu(1). In the former, the axial angle NC–Cu(2)–ND is 175.7 (2)° while the equatorial angles are 104.1 (2), 123.0 (2), and 132.9 (2)°. More significantly, Cu(2) lies only 0.02 Å out of the equatorial plane defined by O, NC', ND', while NC and ND lie 1.97 and 1.94 Å above and below the plane, respectively. At Cu(1), the axial angle NA'–Cu(1)–NB is 173.6 (3)° while the equatorial angles are 88.1 (2), 117.6 (2), and 154.2 (3)°. The central atom Cu(1) lies 0.04 Å out of the equatorial plane. The reason for this greater distortion at Cu(1) is apparent from an examination of Figure 3, in which it can be seen that a perchlorate oxygen atom approaches this copper center in a sixth site, thereby causing a distortion toward tetragonal-pyramidal geometry. The Cu(1)–OCl(13) distance of 3.047 (9) Å is too long to be considered a Cu–O bond and is longer than the values of 2.562–2.883 Å which have been reported[27-30] for "semicoordinated"[31] perchlorate groups; it is, however, apparent that this relatively close approach of the perchlorate group is responsible for the distortion observed at Cu(1). A possible alternate description of the geometry at Cu(1) as a tetragonal pyramid with NA apical is not appealing. The four atoms O, Na', NB, and NB' are far from coplanar, with O and NB' lying 0.24 and 0.25 Å, respectively, below the least-squares plane while NA' and NB' lie 0.23 and 0.26 Å, respectively, above it. It is true that, as expected[32] for a tetragonal pyramid, the central copper atom lies 0.18 Å above the plane (i.e., toward the apical atom).

The four axial Cu–N distances are in the range 1.999 (6)–2.012 (7) Å. The equatorial distances show a wider variation, with values of 2.043 (6)–2.246 (6) Å; this longest bond is the Cu(1)–NA bond which is opposite the perchlorate site. These bond lengths can be compared to the values of 1.958–2.123 Å in the other trigonal-bipyramidal 2,2'-bipyridine complexes of copper(II) whose structures have been well characterized.[33-37] The axial Cu–N

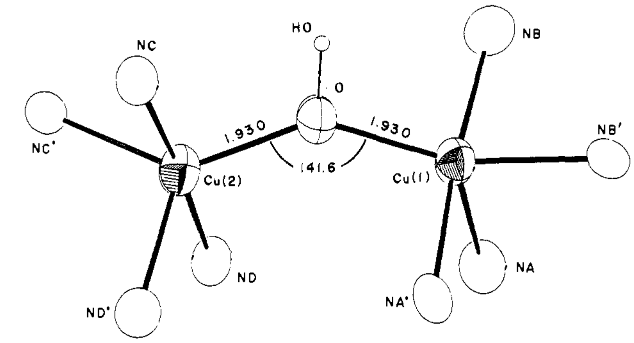


Figure 2. Coordination geometry about the copper(II) ions in $[(bpy)_2Cu-OH-Cu(bpy)_2]^{3+}$. Atoms NA and NA' are nitrogen atoms of pyridine groups A and A', respectively, and are parts of the same bipyridine ligand etc.

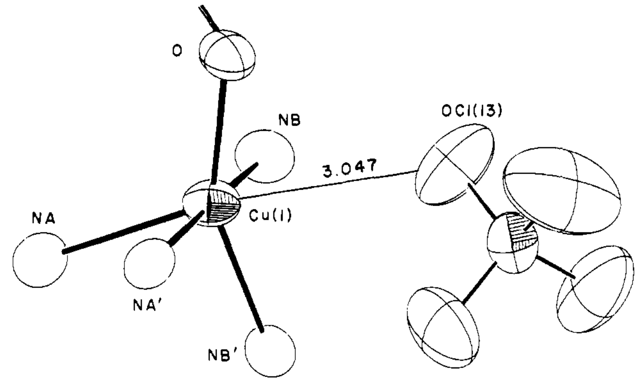


Figure 3. Coordination geometry about Cu(1), showing the interaction between Cu(1) and O(13) which leads to a distortion of the trigonal-bipyramidal geometry about Cu(1) (see text).

(26) Supplementary material.

(27) Lewis, D. L.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1972**, *11*, 2216.

(28) Lewis, D. L.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 143.

(29) Lewis, D. L.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 147.

(30) Lewis, D. L.; McGregor, K. T.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 1013.

(31) Brown, D. S.; Lee, J. D.; Melson, B. G. A.; Hathaway, B. J.; Procter, I. M.; Tomlinson, A. A. G. *Chem. Commun.* **1967**, 369.

(32) Brown, D. S.; Einstein, F. W. B.; Tuck, D. G. *Inorg. Chem.* **1969**, *8*, 14. Hodgson, D. J.; Ibers, J. A. *Ibid.* **1969**, *8*, 1282. Phelps, D. W. J.; Goodman, W. H.; Hodgson, D. J. *Ibid.* **1976**, *15*, 2266.

(33) Harrison, W. D.; Hathaway, B. J.; Kennedy, D. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2301. Harrison, W. D.; Hathaway, B. J. *Ibid.* **1979**, *B35*, 2910.

(34) Stephens, F. S.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2293.

Table I. Final Positional Parameters for $[(bpy)_2Cu\text{-}OH\text{-}Cu(bpy)_2](ClO_4)_3$[a]

atom	x	y	z	atom	x	y	z
Cu(1)	0.23765 (1)	0.16054 (5)	0.05186 (5)	CC(3')	0.3146 (6)	0.2253 (5)	−0.3897 (5)
Cu(2)	0.34106 (6)	0.22174 (5)	−0.13232 (5)	CC(4')	0.2864 (6)	0.2948 (5)	−0.4100 (6)
O	0.2733 (4)	0.1632 (3)	−0.0590 (3)	CC(5')	0.2702 (6)	0.3455 (5)	−0.3545 (5)
Cl(1)	0.16645 (15)	0.45953 (12)	0.45219 (14)	CC(6')	0.2854 (5)	0.3267 (5)	−0.2719 (5)
O(11)	0.1288 (6)	0.4980 (4)	0.3864 (5)	ND	0.3075 (42)	0.3147 (33)	−0.0761 (34)
O(12)	0.2158 (7)	0.4014 (4)	0.4236 (6)	CD(2)	0.3750 (5)	0.3554 (4)	−0.0437 (5)
O(13)	0.2231 (6)	0.5038 (4)	0.5008 (6)	CD(3)	0.3576 (6)	0.4216 (5)	−0.0033 (5)
O(14)	0.1005 (8)	0.4322 (8)	0.4982 (6)	CD(4)	0.2683 (6)	0.4425 (5)	0.0012 (6)
Cl(2)	0.4252 (2)	0.1557 (2)	0.4080 (2)	CD(5)	0.2004 (6)	0.4023 (5)	−0.0318 (5)
O(21)	0.4896 (8)	0.1822 (8)	0.4575 (8)	CD(6)	0.2218 (6)	0.3372 (5)	−0.0704 (5)
O(22)	0.3594 (6)	0.2087 (7)	0.3864 (8)	ND'	0.4702 (41)	0.2664 (35)	−0.0999 (36)
O(23)	0.4544 (8)	0.1253 (8)	0.3402 (6)	CD(2')	0.4659 (5)	0.3276 (4)	−0.0560 (5)
O(24)	0.3785 (10)	0.1040 (8)	0.4502 (7)	CD(3')	0.5444 (7)	0.3623 (5)	−0.0255 (6)
Cl(3)	0.12116 (18)	0.05001 (16)	−0.30612 (22)	CD(4')	0.6270 (7)	0.3323 (6)	−0.0436 (6)
O(31)	0.1075 (10)	0.0968 (9)	−0.2492 (7)	CD(5')	0.6319 (7)	0.2710 (5)	−0.0892 (6)
O(32)	0.1591 (8)	−0.0136 (6)	−0.2821 (9)	CD(6')	0.5512 (6)	0.2384 (5)	−0.1160 (5)
O(33)	0.0367 (6)	0.0379 (6)	−0.3483 (7)	HO	0.2462	0.1132	−0.0866
O(34)	0.1719 (5)	0.0834 (6)	−0.3654 (6)	HA(3)	0.3148	0.3629	0.2533
NA	0.2051 (4)	0.2680 (3)	0.1107 (4)	HA(4)	0.1700	0.4172	0.2607
CA(2)	0.2751 (5)	0.2916 (4)	0.1576 (5)	HA(5)	0.0532	0.3773	0.1768
CA(3)	0.2649 (7)	0.3465 (5)	0.2159 (6)	HA(6)	0.0719	0.2812	0.0861
CA(4)	0.1788 (8)	0.3777 (6)	0.2205 (7)	HA(3')	0.4466	0.3300	0.2054
CA(5)	0.1107 (8)	0.3549 (6)	0.1735 (7)	HA(4')	0.5800	0.2685	0.1773
CA(6)	0.1236 (7)	0.2985 (5)	0.1196 (6)	HA(5')	0.5742	0.1643	0.0950
NA'	0.3584 (38)	0.1967 (32)	0.0953 (35)	HA(6')	0.4323	0.1200	0.0427
CA(2')	0.3620 (5)	0.2568 (4)	0.1433 (4)	HB(3)	−0.0587	0.0526	0.1075
CA(3')	0.4434 (6)	0.2853 (5)	0.1741 (5)	HB(4)	−0.1294	0.0774	−0.0190
CA(4')	0.5232 (7)	0.2495 (6)	0.1549 (6)	HB(5)	−0.0499	0.1318	−0.1229
CA(5')	0.5191 (6)	0.1887 (5)	0.1072 (5)	HB(6)	0.1046	0.1672	−0.0937
CA(6')	0.4354 (5)	0.1636 (4)	0.0772 (5)	HB(3')	0.0238	0.0313	0.2214
NB	0.1110 (45)	0.1286 (38)	0.0199 (40)	HB(4')	0.1194	0.0111	0.3328
CB(2)	0.0673 (6)	0.0971 (4)	0.0785 (5)	HB(5')	0.2656	0.0553	0.3392
CB(3)	−0.0262 (7)	0.0760 (6)	0.0643 (6)	HB(6')	0.3185	0.1202	0.2248
CB(4)	−0.0644 (8)	0.0913 (6)	−0.0104 (7)	HC(3)	0.3682	0.0799	−0.3824
CB(5)	−0.0201 (8)	0.1210 (7)	−0.0696 (7)	HC(4)	0.4268	−0.0282	−0.3251
CB(6)	0.0704 (7)	0.1423 (6)	−0.0533 (7)	HC(5)	0.4526	−0.0344	−0.1817
NB'	0.2034 (38)	0.1091 (31)	0.1561 (35)	HC(6)	0.4227	0.0716	−0.1049
CB(2')	0.1181 (6)	0.0845 (4)	0.1539 (5)	HC(3')	0.3262	0.1876	−0.4310
CB(3')	0.0848 (7)	0.0493 (6)	0.2230 (7)	HC(4')	0.2754	0.3064	−0.4674
CB(4')	0.1403 (8)	0.0385 (6)	0.2884 (7)	HC(5')	0.2498	0.3942	−0.3694
CB(5')	0.2277 (7)	0.0627 (6)	0.2910 (6)	HC(6')	0.2761	0.3633	−0.2305
CB(6')	0.2577 (6)	0.1003 (4)	0.2230 (5)	HD(3)	0.4054	0.4511	0.0207
NC	0.3772 (40)	0.1336 (33)	−0.1954 (35)	HD(4)	0.2541	0.4876	0.0272
CC(2)	0.3627 (5)	0.1372 (4)	−0.2764 (4)	HD(5)	0.1381	0.4179	−0.0288
CC(3)	0.3804 (6)	0.0771 (5)	−0.3242 (5)	HD(6)	0.1738	0.3067	−0.0938
CC(4)	0.4131 (6)	0.0141 (5)	−0.2900 (6)	HD(3')	0.5417	0.4061	0.0087
CC(5)	0.4293 (6)	0.0107 (5)	−0.2085 (6)	HD(4')	0.6816	0.3561	−0.0240
CC(6)	0.4104 (6)	0.0718 (5)	−0.1626 (5)	HD(5')	0.6888	0.2513	−0.1061
NC'	0.3133 (38)	0.2594 (32)	−0.2500 (33)	HD(6')	0.5538	0.1930	−0.1475
CC(2')	0.3293 (5)	0.2086 (4)	−0.3066 (4)				

[a] Figure 1 should be consulted for the letter designations of the bpy rings. The numbers in parentheses are errors in the last significant digit(s).

distances (1.96–1.99 Å) were also found to be considerably shorter than the equatorial distances (2.06–2.11 Å); a similar axial contraction is observed in $CuCl_5^{3-}$, $CuBr_5^{3-}$, and related species.[38,39] With the exception of the long Cu(1)–NA bond of 2.246 Å, the Cu–N distances in the present complex are similar to those in other copper(II)–bipyridine complexes; it is noteworthy that in $Cu(bpy)_3^{2+}$ there is one Cu–N distance of 2.45 Å which is considerably longer than the Cu(1)–NA distance observed here. The Cu–N bond lengths here are no shorter than the values observed in a variety of substituted amine complexes,[3,40] which suggests that there is little multiple bonding between the metal atoms and the aromatic ligands; similar observations have been made for ruthenium(III) complexes of bipyridine[41] and for chromium(III) complexes of the related 1,10-phenanthroline ligand.[42,43]

The Cu–O bridging distances of 1.930 (5) and 1.930 (5) Å are evidently symmetric. While we are unaware of any other singly bridged binuclear Cu–OH–Cu system whose structure has been determined, the present values are comparable to those of 1.941–1.989 Å reported[44–49] in singly bridged Cr(III)–OH–Cr(III)

(35) Stephens, F. S. J. Chem. Soc., Dalton Trans. 1972, 1350.
(36) Kaiser, J.; Brauer, G.; Schroder, F. A.; Taylor, I. F.; Rasmussen, S. E. J. Chem. Soc., Dalton Trans. 1974, 1490.
(37) Ferrari, M. B.; Corradi, A. B.; Fava, G. G.; Palmieri, C. G.; Nardelli, M.; Pelizzi, C. Acta Crystallogr., Sect. B 1973, B29, 1808.
(38) Raymond, K. N.; Meek, D. W.; Ibers, J. A. Inorg. Chem. 1968, 7, 1111.
(39) Goldfield, S. A.; Raymond, K. N. Inorg. Chem. 1971, 10, 2604.
(40) Hodgson, D. J. Prog. Inorg. Chem. 1977, 23, 211 and references therein.
(41) Phelps, D. W.; Kahn, E. M.; Hodgson, D. J. Inorg. Chem. 1975, 14, 2486.
(42) Veal, J. T.; Hatfield, W. E.; Hodgson, D. J. Acta Crystallogr., Sect. B 1973, B29, 12.
(43) Scaringe, R. P.; Singh, P.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. 1975, 14, 1127.
(44) Veal, J. T.; Jeter, D. Y.; Hempel, J. C.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. Inorg. Chem. 1973, 12, 2928.
(45) Engel, P.; Gudel, H. U. Inorg. Chem. 1977, 16, 1589.
(46) Hodgson, D. J.; Pedersen, E., submitted for publication.
(47) Cline, S. J.; Hodgson, D. J.; Glerup, J.; Pedersen, E., submitted for publication.
(48) Kaas, K. Acta Crystallogr., Sect. B 1979, B35, 596.

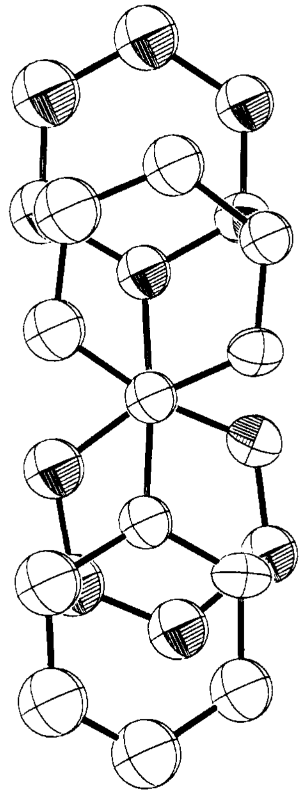


Figure 4. Overlap between bipyridine A–A′ and bipyridine D–D′ in $[(bpy)_2Cu\text{–}OH\text{–}Cu(bpy)_2]^{3+}$, as viewed normal to the D ring. The shaded ellipsoids correspond to the D and D′ ring atoms.

and to values of 1.895–1.948 Å in the doubly hydroxo-bridged copper(II) dimers;[50] all of these distances are considerably longer than those found in linear Cr–O–Cr systems[51,52] which suggests that there is no multiple bonding between the metal atoms and the bridging oxygen atom.

The Cu–O–Cu bridging angle of 141.6 (3)° is in the range of 135.4–165.6° reported for single hydroxo-bridged Cr(III) complexes.[44–49] As can be seen in Figure 1, and more clearly in Figure 4, the observed bridging geometry permits (or causes) one of the bpy ligands on the Cu(1) to lie approximately parallel to one on C(2), with an average interplanar separation of approximately 3.5 Å. This observed interplanar separation is similar to that observed in a number of purines[53] and aromatic molecular complexes[54] and is suggestive of some π–π attraction between the A and D groups. It is noteworthy that a similar interaction was observed in our study of an oxo-bridged ruthenium(III) dimer.[41] It is clear from an examination of Figure 4 that the overlap between the rings is such as to position the polar nitrogen atom directly over the π cloud of the adjacent ring which optimizes a dipole-induced dipole interaction. This type of stacking interaction is seen in a number of purines and purine derivatives.[53] The group itself is significantly distorted from planarity (vide infra), but ring A′ evidently lies over ring D′ and the interplanar angle between these two rings is only 3.6°. On the basis of this structural experiment, of course, we are not able to conclude to what extent (if any) this postulated ligand–ligand interaction influences the bridging geometry. There is clearly no Cu(1)–Cu(2) bond, the Cu(1)–Cu(2) separation being 3.645 (2) Å. The bond lengths and bond angles in the complex are tabulated in Tables II and III.

(49) Kaas, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1603.
(50) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
(51) Urushiyamma, A.; Nomura, T.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3971.
(52) Yevitz, M.; Stanko, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1512.
(53) Bugg, C. E. *Jerusalem Symp. Quantum Chem. Biochem.* **1972**, *4*, 178.
(54) Herbstein, F. H. *Perspect. Struct. Chem.* **1971**, *4*, 166.

Table II. Principal Interatomic Distances (Å) for $[(bpy)_2Cu\text{-}OH\text{-}Cu(bpy)_2](ClO_4)_3$

Cu(1)–Cu(2)	3.645 (2)	NA–NA′	2.642 (8)
Cu(1)–O	1.930 (5)	NA–CA(2)	1.334 (9)
Cu(1)–NA	2.246 (6)	NA–CA(6)	1.346 (11)
Cu(1)–NA′	2.008 (6)	CA(2)–CA(3)	1.400 (11)
Cu(1)–NB	2.012 (7)	CA(2)–CA(2′)	1.467 (10)
Cu(1)–NB′	2.043 (6)	CA(3)–CA(4)	1.403 (14)
Cu(1)–O(13)	3.047 (9)	CA(4)–CA(5)	1.310 (13)
Cu(2)–O	1.930 (5)	CA(5)–CA(6)	1.377 (13)
Cu(2)–NC	1.999 (6)	NA′–CA(2′)	1.349 (9)
Cu(2)–NC′	2.079 (6)	NA′–CA(6′)	1.338 (9)
Cu(2)–ND	2.005 (6)	CA(2′)–CA(3′)	1.387 (11)
Cu(2)–ND′	2.125 (6)	CA(3′)–CA(4′)	1.401 (13)
Cl(1)–O(11)	1.386 (7)	CA(4′)–CA(5′)	1.358 (12)
Cl(1)–O(12)	1.383 (8)	CA(5′)–CA(6′)	1.391 (11)
Cl(1)–O(13)	1.389 (7)	NB–NB′	2.596 (9)
Cl(1)–O(14)	1.362 (9)	NB–CB(2)	1.322 (10)
Cl(2)–O(21)	1.312 (10)	NB–CB(6)	1.345 (12)
Cl(2)–O(22)	1.406 (10)	CB(2)–CB(3)	1.448 (12)
Cl(2)–O(23)	1.337 (9)	CB(2)–CB(2′)	1.439 (11)
Cl(2)–O(24)	1.379 (12)	CB(3)–CB(4)	1.360 (14)
Cl(3)–O(31)	1.291 (11)	CB(4)–CB(5)	1.319 (14)
Cl(3)–O(32)	1.337 (8)	CB(5)–CB(6)	1.411 (14)
Cl(3)–O(33)	1.420 (10)	NB′–CB(2′)	1.342 (9)
Cl(3)–O(34)	1.403 (8)	NB′–CB(6′)	1.343 (9)
O–HO	1.08	CB(2′)–CB(3′)	1.418 (12)
NC–NC′	2.619 (8)	CB(3′)–CB(4′)	1.338 (13)
NC–CC(2)	1.344 (8)	CB(4′)–CB(5′)	1.368 (14)
NC–CC(6)	1.332 (10)	CB(5′)–CB(6′)	1.405 (12)
CC(2)–CC(3)	1.382 (10)	ND–ND′	2.618 (9)
CC(2)–CC(2′)	1.469 (10)	ND–CD(2)	1.335 (9)
CC(3)–CC(4)	1.356 (11)	ND–CD(6)	1.343 (10)
CC(4)–CC(5)	1.356 (12)	CD(2)–CD(3)	1.408 (11)
CC(5)–CC(6)	1.382 (12)	CD(2)–CD(2′)	1.464 (10)
NC′–CC(2′)	1.343 (9)	CD(3)–CD(4)	1.385 (12)
NC′–CC(6′)	1.337 (9)	CD(4)–CD(5)	1.340 (12)
CC(2′)–CC(3′)	1.409 (10)	CD(5)–CD(6)	1.388 (11)
CC(3′)–CC(4′)	1.369 (11)	ND′–CD(2′)	1.331 (9)
CC(4′)–CC(5′)	1.330 (12)	ND′–CD(6′)	1.345 (10)
CC(5′)–CC(6′)	1.412 (11)	CD(2′)–CD(3′)	1.396 (11)
		CD(3′)–CD(4′)	1.388 (13)
		CD(4′)–CD(5′)	1.350 (13)
		CD(5′)–CD(6′)	1.388 (12)

The geometries of the eight pyridine rings in the structure are normal. Thus, the average bond lengths for the C–N and C–C bonds in the rings are not significantly different from those reported elsewhere for a variety of substituted pyridine complexes.[41] Similarly, the C(2)–C(2)′ distances of 1.439 (11)–1.469 (10) Å, with an average of 1.460 (14) Å, are similar to those in other bipyridine complexes.[33,41] The eight pyridine rings do not deviate significantly from planarity, with no atom more than 0.02 Å from the six-atom least-squares plane. One of the bipyridine groups, however, is considerably distorted from planarity, the dihedral angle between the pairs of planar pyridine rings being 12.4° for the A group; the torsion around the C(2)–C(2)′ bond in the other three bipyridine groups is much smaller, the dihedral angles ranging from 3.4 to 4.7°. Dihedral angles as large as 31° have been reported for bpy complexes, the average value in a recent survey being 8°.[55] The four independent N–Cu–N chelating angles range from 76.6 (2) to 79.9 (2)° with an average value of 78.7°, and the N···N "bites" range from 2.60 to 2.64 Å with an average of 2.62 (2) Å; these values are again similar to those in other systems.[41,55]

As was noted above, the perchlorate groups are undergoing considerable thermal motion. Consequently, the calculated Cl–O bond lengths of 1.29–1.42 Å, with an average of 1.37 (4) Å, are relatively imprecisely determined and are shorter than normal. These distances can be "corrected" for thermal motion by using the riding model of Busing and Levy,[56] which leads to an average

(55) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.*, in press and references therein.
(56) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142.

Table III. Principal Interatomic Angles (Deg) for $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$

O(13)–Cu(1)–O	71.8 (2)	O(11)–Cl(1)–O(12)	108.6 (5)	CB(2)–NB–CB(6)	121.5 (8)	NC–CC(2)–CC(3)	120.2 (7)
O(13)–Cu(1)–NA	170.6 (2)	O(11)–Cl(1)–O(13)	111.6 (6)	Cu(1)–NB′–CB(2′)	113.8 (5)	NC–CC(2)–CC(2′)	114.5 (6)
O(13)–Cu(1)–NA′	103.2 (2)	O(11)–Cl(1)–O(14)	110.3 (6)	Cu(1)–NB′–CB(6′)	125.6 (5)	CC(3)–CC(2)–CC(2′)	125.3 (7)
O(13)–Cu(1)–NB	81.0 (2)	O(12)–Cl(1)–O(13)	108.9 (5)	CB(2′)–NB′–CB(6′)	120.5 (7)	CC(2)–CC(3)–CC(4)	120.4 (8)
O(13)–Cu(1)–NB′	82.5 (2)	O(12)–Cl(1)–O(14)	108.6 (8)	Cu(2)–NC–CC(2)	116.4 (5)	CC(3)–CC(4)–CC(5)	119.6 (9)
O–Cu(1)–NA	117.6 (2)	O(13)–Cl(1)–O(14)	108.6 (6)	Cu(2)–NC–CC(6)	124.7 (5)	CC(4)–CC(5)–CC(6)	118.4 (9)
O–Cu(1)–NA′	92.7 (2)	O(21)–Cl(2)–O(22)	112.2 (8)	CC(2)–NC–CC(6)	118.8 (6)	NC–CC(6)–CC(5)	122.6 (8)
O–Cu(1)–NB	93.2 (2)	O(21)–Cl(2)–O(23)	114.5 (9)	Cu(2)–NC′–CC(2′)	112.9 (5)	NC′–CC(2′)–CC(2)	116.2 (6)
O–Cu(1)–NB′	154.2 (2)	O(21)–Cl(2)–O(24)	107.7 (9)	Cu(2)–NC′–CC(6′)	126.8 (5)	NC′–CC(2′)–CC(3′)	120.3 (7)
NA–Cu(1)–NA′	76.6 (2)	O(22)–Cl(2)–O(23)	108.8 (7)	CC(2′)–NC′–CC(6′)	120.3 (6)	CC(2)–CC(2′)–CC(3′)	123.5 (7)
NA–Cu(1)–NB	98.4 (2)	O(22)–Cl(2)–O(24)	103.6 (9)	Cu(2)–ND–CD(2)	117.0 (5)	CC(2′)–CC(3′)–CC(4′)	117.8 (8)
NA–Cu(1)–NB′	88.1 (2)	O(23)–Cl(2)–O(24)	109.4 (9)	Cu(2)–ND–CD(6)	123.2 (5)	CC(3′)–CC(4′)–CC(5′)	122.4 (9)
NA′–Cu(1)–NB	173.6 (3)	O(31)–Cl(3)–O(32)	115.7 (10)	CD(2)–ND–CD(6)	119.8 (7)	CC(4′)–CC(5′)–CC(6′)	118.1 (8)
NA′–Cu(1)–NB′	96.0 (2)	O(31)–Cl(3)–O(33)	107.0 (10)	Cu(2)–ND′–CD(2′)	112.9 (5)	NC′–CC(6′)–CC(5′)	121.0 (7)
NB–Cu(1)–NB′	79.6 (2)	O(31)–Cl(3)–O(34)	109.3 (11)	Cu(2)–ND′–CD(6′)	127.5 (5)	ND–CD(2)–CD(3)	120.8 (7)
O–Cu(2)–NC	92.6 (2)	O(32)–Cl(3)–O(33)	111.0 (8)	CD(2′)–ND′–CD(6′)	119.5 (7)	ND–CD(2)–CD(2′)	115.6 (7)
O–Cu(2)–NC′	132.9 (2)	O(32)–Cl(3)–O(34)	110.4 (7)	NA–CA(2)–CA(3)	121.4 (8)	CD(3)–CD(2)–CD(2′)	123.6 (7)
O–Cu(2)–ND	91.6 (2)	O(33)–Cl(3)–O(34)	102.5 (6)	NA–CA(2)–CA(2′)	115.7 (7)	CD(2)–CD(3)–CD(4)	117.3 (8)
O–Cu(2)–ND′	123.0 (2)	Cu(1)–O–Cu(2)	141.6 (3)	CA(3)–CA(2)–CA(2′)	123.0 (8)	CD(3)–CD(4)–CD(5)	122.0 (9)
NC–Cu(2)–NC′	79.9 (2)	Cu(1)–O–HO	105.2	CA(2)–CA(3)–CA(4)	117.1 (9)	CD(4)–CD(5)–CD(6)	117.9 (8)
NC–Cu(2)–ND	175.7 (2)	Cu(2)–O–HO	113.2	CA(3)–CA(4)–CA(5)	121.2 (11)	ND–CD(6)–CD(5)	122.1 (8)
NC–Cu(2)–ND′	100.1 (2)	CB(3)–CB(2)–CB(2′)	123.6 (8)	CA(4)–CA(5)–CA(6)	119.3 (11)	ND′–CD(2′)–CD(2)	115.7 (7)
NC′–Cu(2)–ND	96.4 (2)	CB(2)–CB(3)–CB(4)	116.4 (10)	NA–CA(6)–CA(5)	122.2 (9)	ND′–CD(2′)–CD(3′)	120.8 (8)
NC′–Cu(2)–ND′	104.1 (2)	CB(3)–CB(4)–CB(5)	123.6 (11)	NA′–CA(2′)–CA(2)	115.8 (7)	CD(2)–CD(2′)–CD(3′)	123.4 (8)
NC–Cu(2)–ND′	78.6 (2)	CB(4)–CB(5)–CB(6)	118.5 (11)	NA′–CA(2′)–CA(3′)	121.7 (7)	CD(2′)–CD(3′)–CD(4′)	118.3 (9)
Cu(1)–NA–CA(2)	110.7 (5)	NB–CB(6)–CB(5)	119.9 (10)	CA(2)–CA(2′)–CA(3′)	122.4 (8)	CD(3′)–CD(4′)–CD(5′)	121.2 (10)
Cu(1)–NA–CA(6)	128.3 (6)	NB′–CB(2′)–CB(2)	115.0 (7)	CA(2′)–CA(3′)–CA(4′)	118.3 (9)	CD(4′)–CD(5′)–CD(6′)	117.4 (9)
CA(2)–NA–CA(6)	118.8 (7)	NB′–CB(2′)–CB(3′)	119.6 (7)	CA(3′)–CA(4′)–CA(5′)	119.7 (9)	ND′–CD(6′)–CD(5′)	122.7 (8)
Cu(1)–NA′–CA(2′)	118.9 (5)	CB(2)–CB(2′)–CB(3′)	125.3 (8)	CA(4′)–CA(5′)–CA(6′)	119.1 (1)		
Cu(1)–NA′–CA(6′)	121.9 (5)	CB(2′)–CB(3′)–CB(4′)	119.4 (10)	NA′–CA(6′)–CA(5′)	122.0 (7)		
CA(2′)–NA′–CA(6′)	119.2 (6)	CB(3′)–CB(4′)–CB(5′)	121.5 (1)	NB–CB(2)–CB(3)	119.9 (8)		
Cu(1)–NB–CB(2)	114.8 (5)	CB(4′)–CB(5′)–CB(6′)	117.9 (9)	NB–CB(2)–CB(2′)	116.4 (8)		
Cu(1)–NB–CB(6)	123.5 (7)	NB′–CB(6′)–CB(5′)	121.9 (8)				

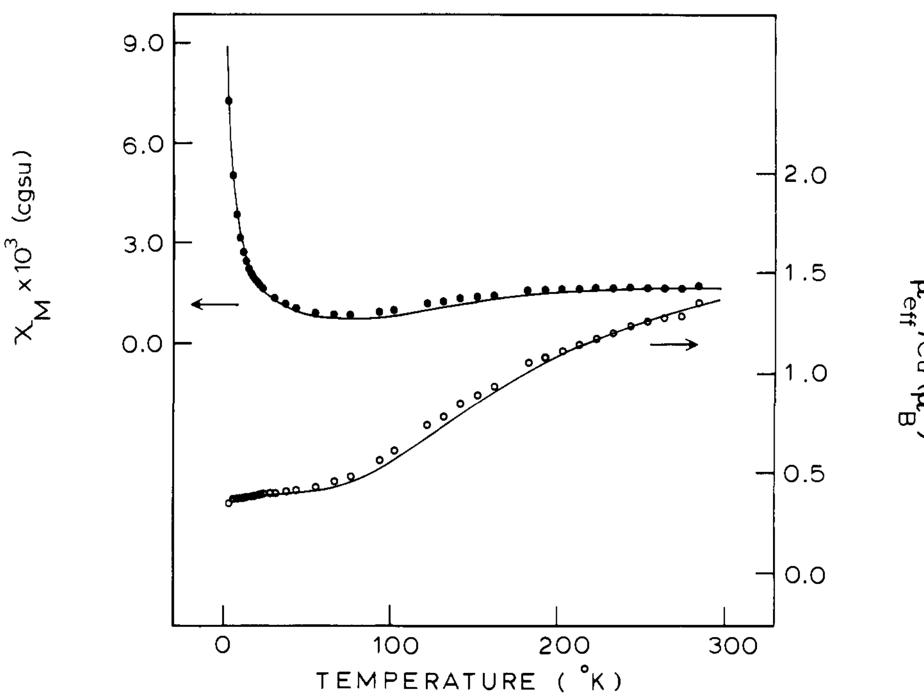


Figure 5. Molar paramagnetic susceptibility, χ_M, of the binuclear complex and effective magnetic moment per copper(II) ion, μ_{eff}/Cu, vs. temperature curves for a solid sample of $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$. The solid lines result from a least-squares fit of the data to the theoretical equation.

"corrected" value of 1.49 (4) Å.

There is no evidence for hydrogen bonding in the crystals. The only potential donor in the complex is the bridging hydroxyl group, and this does not closely approach any acceptor site.

Infrared Spectroscopy. The KBr-pellet IR spectrum of either of the two $[(L)_2Cu-OH-Cu(L)_2](ClO_4)_2$ (L = bpy or phen) compounds shows a relatively broad and medium-intensity band at 3560 cm^{-1}. This is close to the OH band position reported[9] for $[(tren)Cu-OH-Cu(tren)]X_3$, where X is either PF_6^- or ClO_4^-. The assignment of the O–H stretch was substantiated for the PF_6^- compound by preparing the corresponding deuterated compound, $[(tren\text{-}d_6)Cu-OD-Cu(tren\text{-}d_6)](PF_6)_3$. The reported OH band shifted from 3601 to 2656 cm^{-1}.

Magnetic Susceptibility. Variable-temperature magnetic susceptibility data were collected for both $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ and $[(phen)_2Cu-OH-Cu(phen)_2](ClO_4)_3$ in the temperature range 4.2–286 K. Figures 5 and 6 illustrate the data for these two complexes; the data are given in Tables IV and V.[26] Strong antiferromagnetic exchange interactions are present as evidenced by the fact that the effective magnetic moment per

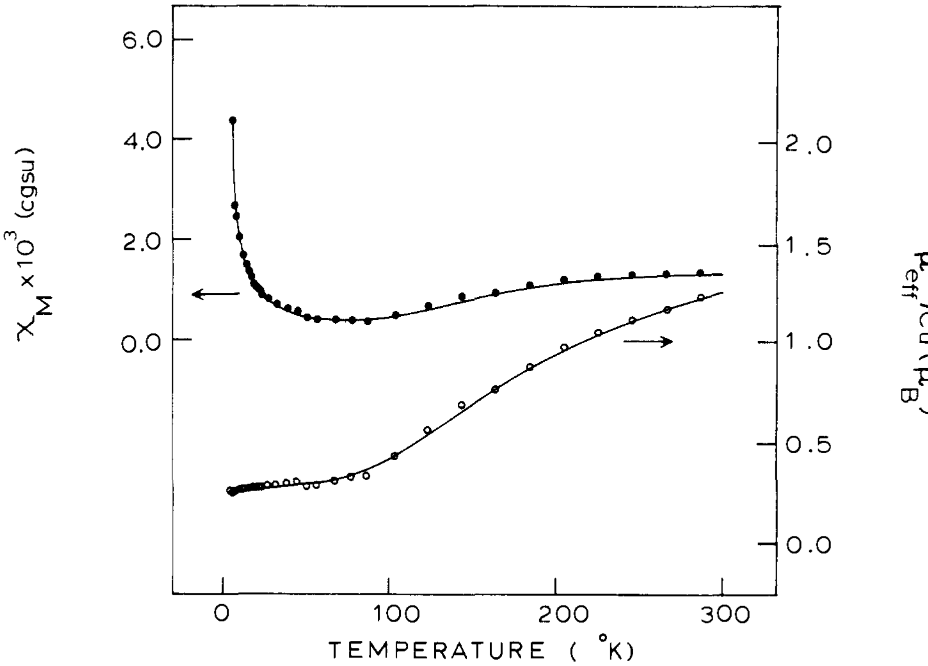


Figure 6. Molar paramagnetic susceptibility, χ_M, of the binuclear complex and effective magnetic moment per copper(II) ion, μ_{eff}/Cu, vs. temperature curves for a solid sample of $[(phen)_2Cu-OH-Cu(phen)_2](ClO_4)_3$. The solid lines result from a least-squares fit of the data to the theoretical equation.

copper(II) ion is less than the spin-only value of 1.73 μ_B even at 286 K. For example, μ_{eff}/Cu is 1.33 μ_B for the bpy complex at 286 K and drops to a value of 0.35 μ_B at 4.2 K.

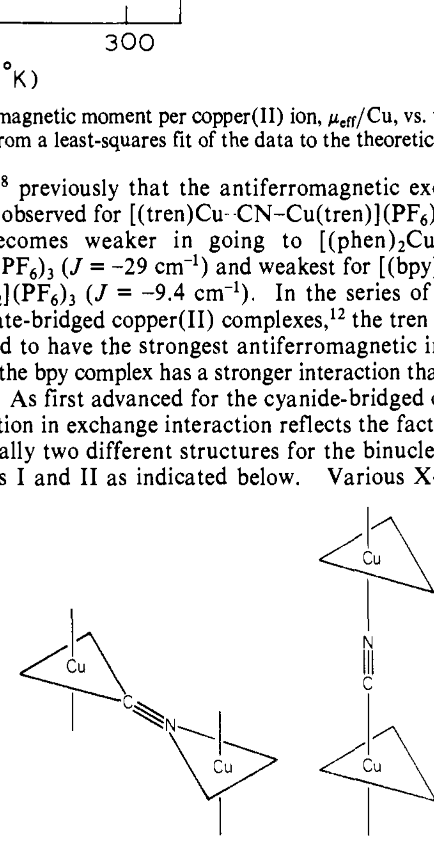
The magnetic susceptibility data for the two complexes were least-squares fit to the Bleaney–Bowers equation (eq 1),[57] which

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3 + \exp(-2J/kT)}\right] + N\alpha + (PAR)(4.2/T) \qquad (1)$$

gives the molar paramagnetic susceptibility, χ_M, for a $S_1 = S_2 = {}^1/_2$ binuclear complex experiencing an isotropic exchange interaction (spin Hamiltonian is $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$). In this equation, $2J$ is the energy separation between the $S = 0$ and $S = 1$ states of the binuclear complex and the other symbols have their usual meaning. The temperature-independent paramagnetism for a binuclear copper(II) complex, $N\alpha$, was taken as 120×10^{-6} cgsu/mol. The third term in the expression which incorporates the parameter *PAR* takes account of the presence of a small amount of a paramagnetic impurity. This is especially important for strongly interacting systems where the contribution to the measured susceptibility from the paramagnetic impurities becomes significant at low temperatures. As can be seen in both Figures 5 and 6, there is a marked increase in χ_M below ca. 25 K for both compounds which is the signature for the presence of a small amount of an unavoidable paramagnetic impurity. *PAR* is the susceptibility for this impurity at 4.2 K. Broad weak signals were seen in EPR spectra which could be attributed to the impurities.

The least-squares fitting parameters for $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ were found to be $J = -161$ cm^{-1} and $g = 2.00$ with *PAR* fixed at 0.009 cgsu. In the case of the phen complex, the parameters are $J = -177$ cm^{-1} and $g = 2.00$ with *PAR* in this case fixed at 0.004 cgsu. The solid lines in Figures 5 and 6 represent these two least-squares fits to the theoretical equation, which can be seen to be good.

It is immediately apparent that the antiferromagnetic exchange interaction is appreciably weaker in the bpy and phen single hydroxo-bridged complexes than was found[9] for the two $[(tren)Cu-OH-Cu(tren)]X_3$ complexes, where $J = -350$ cm^{-1} for the PF_6^- complex and $J = -380$ cm^{-1} for the ClO_4^- complex. This change in J values is not surprising in view of the observations reported[58] previously that the antiferromagnetic exchange interaction observed for $[(tren)Cu-CN-Cu(tren)](PF_6)_3$ ($J = -88$ cm^{-1}) becomes weaker in going to $[(phen)_2Cu-CN-Cu(phen)_2](PF_6)_3$ ($J = -29$ cm^{-1}) and weakest for $[(bpy)_2Cu-CN-Cu(bpy)_2](PF_6)_3$ ($J = -9.4$ cm^{-1}). In the series of analogous imidazolate-bridged copper(II) complexes,[12] the tren complex is also found to have the strongest antiferromagnetic interaction; however, the bpy complex has a stronger interaction than the phen complex. As first advanced for the cyanide-bridged complexes, the variation in exchange interaction reflects the fact that there are basically two different structures for the binuclear cations, structures I and II as indicated below. Various X-ray struc-



I II

tures[59–62] have been reported for salts containing $Cu(tren)X^+$ ions. The tripodal ligand tren has a strong tendency to enforce a trigonal-bipyramidal coordination geometry and leaves one axial site vacant. The copper(II) ion orbital ground state for this geometry is d_{z^2} with the z axis aligned along the axial direction. In short, the tren complexes adopt structure II whereas the bpy and phen complexes assume structure I; preliminary structural investigations of $[(tren)Cu-OH-Cu(tren)](ClO_4)_3$ support the assignment of structure II for this complex. In structure II, the copper d_{z^2} orbitals, one on each copper center, are more favorably

(57) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 451.

(58) Bieksza, D. S.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 924.
(59) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1974**, *13*, 1911.
(60) Laskowski, E. J.; Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 2449.
(61) Felthouse, T. R.; Duesler, E. N.; Christensen, A. T.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 245.
(62) Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 724.

positioned to overlap directly in a σ fashion with the bridging moiety. There can be an antiferromagnetic coupling via σ orbitals of the bridge for complexes with structure (II); however, it would not involve the main lobe of the copper(II) d_{z^2} orbitals. The structure of the binuclear cation in $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ approaches the limiting structure I, and this explains why the interaction for this complex is weaker than that observed for the tren single hydroxo-bridged complex.

The Cu-O-Cu bridge angle in $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ is 141.6 (3)°, which is considerably out of the range of bridge angles (95-104°) known for dihydroxo-bridged copper(II) complexes. In the case of the dihydroxo-bridged complexes,[50] the slope of the plot of J vs. bridge angle is -37.3 cm^{-1} deg^{-1} with $J = 0$ for a bridge angle of 97.6°. Bridge angles greater than 97.6° lead to antiferromagnetic interactions. If the data for $[(bpy)_2Cu-OH-Cu(bpy)_2](ClO_4)_3$ fit onto the same correlation line, the exchange parameter J would have been predicted to be -1641 cm^{-1} for the Cu-O-Cu angle found. Instead, a value of -161 cm^{-1} is found. The obvious explanation for this apparent discrepancy lies in the fact that the single hydroxo-bridged complexes have different electronic ground states (trigonal-bipyramidal d_{z^2}) than are present in the dihydroxo-bridged complexes (square-pyramidal $d_{x^2-y^2}$). It would be interesting to prepare and characterize a series of binuclear copper(II) complexes bridged only by a single hydroxide ion where the nonbridging ligands are, for example, various substituted 2,2'-bipyridines, and such a study is being undertaken. With a single hydroxide ion as the only bridge it should be possible to encompass a larger range of bridgehead Cu-O-Cu angles than the 9° range observed for the dihydroxo-bridged complexes; indeed, in the analogous Cr(III) complexes a range of over 30° has already been reported.[44-49] While a linear correlation of J with bridge angle ϕ might not be expected, we anticipate that there will again be a strong correlation between ϕ and J.

Acknowledgment. We are grateful for partial funding from National Institutes of Health Grant HL13652 (D.N.H.).

Supplementary Material Available: Tables of observed and calculated magnetic susceptibility data and thermal parameters and a listing of observed and calculated amplitudes (31 pages). Ordering information is given on any current masthead page.

Electrostatic Ligand-Ligand Interactions in Ternary Amino Acid-Palladium(II) Complexes. Synthetic Studies and Spectroscopic Evidence

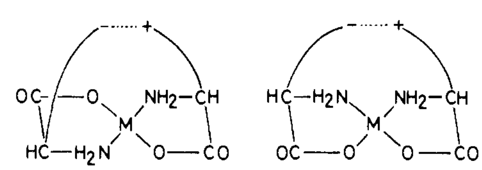
Osamu Yamauchi* and Akira Odani

Contribution from the Faculty of Pharmaceutical Sciences, Osaka University, 133-1 Yamadakami, Suita, Osaka 565, Japan. *Received March 28, 1980*

Abstract: Synthetic and spectroscopic studies have been carried out on electrostatic ligand-ligand interactions in ternary amino acid-palladium(II) complexes containing an acidic amino acid (A) and a basic amino acid (B). Thus, the ternary complexes Pd(A)(L-B)(H), where A refers to L- or D-aspartate, L- or D-glutamate, or L-cysteate and B to argininate with a proton (H) attached to the basic side group, have been isolated as crystals. The circular dichroism spectral magnitudes in the d-d region observed for neutral solutions of Pd(L-A)(L-B)(H) involving argininate or lysinate as B are smaller than the magnitudes estimated from those exhibited by $Pd(L\text{-}A)_2$ and $Pd(L\text{-}B)_2(H)_2$ by assuming the magnitude additivity, whereas the ternary systems without the possibility of ligand-ligand interactions such as Pd(L-A)(L-Ala) (Ala = alaninate) exhibit the spectra with magnitudes close to the estimated ones. ^1H NMR signal patterns and chemical shifts of A in the systems Pd(L- or D-A)(L-B)(H) in neutral solution are significantly different from those of $Pd(L\text{- or }D\text{-}A)_2$ and Pd(L- or D-A)(L-Ala). Calculation of the fractional populations of three staggered rotational isomers of free and coordinated aspartate and cysteate from the α-CH-β-CH_2 coupling constants shows that the population of the isomer with the conformation enabling an electrostatic ligand-ligand interaction increases with addition of methanol and a decrease in temperature, directly reflecting the interactions within the complex molecule. In the absence of palladium(II), the populations remain unaffected. Preferential incorporation of an enantiomer of DL-aspartic acid and DL-arginine are observed in the ternary complex formation with optically pure arginine and aspartic acid, respectively. This supports the NMR study and substantiates the stereoselectivity in the palladium(II) coordination plane due to the ligand-ligand interaction.

A number of transition-metal ions play vital roles in biological processes, often forming active centers of metalloenzymes. In enzyme-metal-substrate (EMS) complexes formed in enzymatic reactions involving metal ions,[1] noncovalent interactions between enzyme and substrate molecules around the central metal ion are essential for the efficiency and specificity of the reactions.[2,3] Structural evidence for EMS complex formation has been provided by the X-ray analysis of the carboxypeptidase A-glycyl-L-tyrosine complex,[3] which demonstrates the molecular arrangement and various enzyme-substrate interactions such as the electrostatic interaction between the carboxylate group of glycyl-L-tyrosine and

Chart I



(1) Mildvan, A. S. In "The Enzymes", 3rd ed.; Boyer, P. D., Ed.; Academic Press: New York, 1970; Vol. II, p 445.
(2) (a) Jencks, W. P. *Adv. Enzymol.* **1975**, *43*, 219-410. (b) Frieden, E. *J. Chem. Educ.* **1975**, *52*, 754-761.
(3) (a) Lipscomb, W. N. *Acc. Chem. Res.* **1970**, *3*, 81-89. (b) Hartsuck, J. A.; Lipscomb, W. N. In "The Enzymes", 3rd ed.; Boyer, P.D., Ed.; Academic Press: New York, 1971; Vol. III, p 1. (c) Quiocho, F. A.; Lipscomb, W. N. *Adv. Protein Chem.* **1971**, *25*, 1-78. (d) Ludwig, M. L.; Lipscomb, W. N. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed; Elsevier: Amsterdam, 1973; Vol. 1, p 438.

