C(8)C(10)–O(2) and C(8)–C(9)–C(10) is 5.0°. The pivot bond C(9)–C(12) bends toward the opposite side of the ortho nitro group and has a tilt angle of 2.6° to the C(8)–C(9)–C(10) plane. All these bending directions are almost perpendicular to the plane of O(1)–Co–O(2). Thermal parameters of the acac ring show slight out-of-plane vibrations of the ring. The aromatic ring is nearly perpendicular to the acac ring. Inspection of the thermal parameters shows that the aromatic ring librates around the pivot bond. The geometry is normal except for that of the ortho nitro group. The group is disordered with a ratio of 50:50.

Since two chelate rings of tren, B and C, are enantiomeric to each other and only ring A contributes to the optical activity, the environment around the cobalt atom is apparently almost symmetric as far as the acac oxygen atoms and tren are concerned. In spite of such structure, the present complex shows significantly large optical rotation. If the above geometry of the complex ion still stands for the average conformation in an aqueous solution, the bent structure of the acac ring should be taken into account for the model of the present series. Not only the disposition of the ortho nitro group and C(18) methyl group but also the bent structure and the disposition of the aromatic ring break the symmetry of coordination sphere. The possible interaction between the ortho nitro group and the amino group may also contribute. These dissymmetric effects seem to be comparable to the dissymmetry of optically active complexes whose activity arises from the chirality within the coordination sphere.

Acknowledgment. The authors express their thanks to Professor Y. Iitaka for the measurements with the diffractometer. This research was supported in part by a Scientific Research Grant from the Ministry of Education to which the authors' thanks are due.

Registry No. [(−)$_{589}$-3-(6-Methyl-2,4-dinitrophenyl)pentane-2,4-dionato][tris(2-aminoethyl)amine]cobalt(III) dibromide dihydrate, 74397-72-1; 3-(6-methyl-2,4-dinitrophenyl)pentane-2,4-dione, 74397-55-0; 1-chloro-6-methyl-2,4-dinitrobenzene, 18905-50-5; 1-fluoro-6-methyl-2,4-dinitrobenzene, 348-97-0; sodium acetylacetonate, 15435-71-9.

Supplementary Material Available: Tables III and V, showing observed and calculated intensity relations between some hkl and $h\bar{k}l$ reflections and relevant interatomic distances less than 3.5 Å outside the complex ions, and a table of observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica dell'Università, Laboratorio CNR, 50132 Firenze, Italy, and the Istituto di Chimica Generale della Factoltà di Farmacia, Università di Firenze, 50121 Firenze, Italy

Crystal and Molecular Structure and ESR Spectra of a Dimeric Dialkoxo-Bridged Five-Coordinate Copper(II) Complex

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Received February 26, 1980

The crystal and molecular structure of bis(*N*,*N*-bis(2-(diethylamino)ethyl)-2-hydroxyethylamino-*O*)dicopper(II) diperchlorate has been determined by X-ray diffractometry data. The crystals are monoclinic, of space group $P2_1/n$, with cell dimensions $a = 9.349$ (2) Å, $b = 17.676$ (4) Å, $c = 11.720$ (3) Å, and $\beta = 93.02$ (2)°. The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional R factor of 0.055 over the 1367 independent observed reflections. The structure consists of dinuclear $[Cu_2(bdhe)_2]^{2+}$ cations, which possess a center of symmetry, and of perchlorate anions. The copper(II) ions achieve five-coordination by sharing the oxygen atoms of the ligand. The arrangement of the ligands around the metal ion is intermediate between a trigonal-bipyramidal and a square-pyramidal model. The copper(II)–copper(II) distance is 3.044 (2) Å. Single-crystal ESR spectra of the zinc(II)-doped complex were recorded in order to relate the structural data to the electronic properties. The anisotropic g values and their principal directions were reproduced through an angular overlap (AO) model. The magnetic susceptibility data are discussed within the same formalism.

Introduction

The attempt to relate the magnetic coupling observed in dinuclear complexes with the structural features of the bridged moieties is one of the main research topics of the last few years.[2–6] The problem has been tackled both theoretically[7–11] and experimentally,[12–14] and several useful correlations are now available.

Two of us recently reported the spectral and magnetic properties of a series of dinuclear 3d metal complexes with *N*,*N*-bis(2-(diethylamino)ethyl)-2-hydroxyethylamine (bdheH), $[M_2(bdhe)_2](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn),[15] and found a large variation in the following values of the magnetic coupling constant J (defined through the Hamiltonian $H = -J(S_1 \cdot S_2)$): -495 cm^{-1} for the copper(II), -35 cm^{-1} for the nickel(II), -17 cm^{-1} for the cobalt(II) complex, and smaller values for the iron(II) and manganese(II) derivatives. The structure of the nickel(II) complex is available,[16] showing that the metal ions are in a distorted trigonal-bipy-

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Table I. Positional Parameters (×10^4), Anisotropic Temperature Factors[a] (×10^3), and Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	701 (1)	531 (1)	886 (1)	43 (1)	37 (1)	43 (1)	−5 (1)	13 (1)	−9 (1)
O(1)	−1053 (6)	−66 (3)	547 (5)	47 (4)	46 (4)	47 (4)	−15 (3)	25 (3)	−19 (3)
N(1)	−313 (8)	865 (4)	2252 (6)	61 (5)	31 (4)	37 (5)	−2 (4)	7 (4)	−1 (4)
N(2)	1413 (8)	1654 (4)	722 (6)	49 (5)	38 (5)	51 (5)	−6 (4)	13 (4)	−4 (4)
N(3)	2228 (8)	−120 (4)	2406 (7)	57 (6)	49 (5)	57 (6)	6 (4)	7 (5)	3 (4)
Cl	6808 (4)	3222 (3)	875 (3)	82 (3)	52 (3)	61 (3)	12 (2)	12 (2)	−2 (3)
O(2)[b]	7799 (22)	3248 (12)	−35 (22)	83 (15)	131 (16)	81 (13)	17 (10)	31 (12)	13 (13)
O(3)	5295 (20)	3316 (10)	482 (16)	78 (14)	129 (14)	122 (12)	8 (11)	−3 (10)	16 (11)
O(4)	6793 (101)	2441 (39)	1000 (62)	132 (33)	31 (36)	212 (47)	−12 (26)	4 (36)	28 (32)
O(5)	7180 (42)	3736 (31)	1687 (43)	129 (29)	36 (32)	104 (31)	19 (23)	−35 (25)	−20 (30)
O(6)	7796 (36)	3301 (34)	1972 (30)	115 (26)	85 (28)	56 (25)	−9 (25)	−9 (19)	−17 (26)
O(7)	5894 (59)	3752 (35)	823 (39)	158 (49)	110 (47)	164 (41)	163 (43)	62 (37)	−30 (32)
O(8)	6462 (129)	2585 (114)	1415 (199)	284 (97)	140 (76)	325 (91)	−115 (84)	−23 (92)	123 (66)
O(9)	7190 (44)	2903 (23)	−36 (41)	101 (28)	111 (30)	105 (25)	45 (21)	3 (23)	−43 (30)
O(10)	7130 (43)	4028 (19)	944 (37)	106 (25)	74 (26)	89 (25)	−7 (18)	−8 (21)	5 (19)
O(11)	7065 (90)	2740 (74)	1653 (131)	154 (57)	183 (51)	64 (79)	83 (51)	34 (48)	63 (50)

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$. [b] The O(2) and O(3) atoms have population parameters of $^2/_3$, whereas the O(4)–O(11) atoms have population parameters of $^1/_3$.

Table II. Positional Parameters (×10^4), Isotropic Temperature Factors (×10^3), and Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U, Å^2
C(1)	−1869 (10)	810 (5)	1900 (8)	49 (3)
C(2)	−2176 (10)	62 (6)	1282 (8)	48 (3)
C(3)	102 (10)	1668 (6)	2520 (8)	51 (3)
C(4)	379 (10)	2073 (5)	1418 (8)	50 (3)
C(5)	29 (11)	355 (6)	3262 (9)	55 (3)
C(6)	1586 (12)	212 (6)	3424 (10)	67 (3)
C(7)	2908 (12)	1798 (6)	1200 (10)	68 (3)
C(8)	4044 (13)	1419 (7)	510 (11)	89 (4)
C(9)	1224 (11)	1895 (6)	−499 (9)	59 (3)
C(10)	1455 (13)	2739 (7)	−708 (11)	87 (4)
C(11)	3810 (14)	−13 (8)	2469 (12)	90 (4)
C(12)	4619 (16)	−393 (8)	3463 (14)	121 (5)
C(13)	1840 (12)	−943 (7)	2343 (10)	67 (3)
C(14)	2551 (13)	−1356 (7)	1395 (11)	84 (4)

ramidal environment. The dinuclear units are centrosymmetric, with two bridging alkoxo groups. As such they are similar to the series of dihydroxo-bridged copper(II) complexes for which Hatfield and Hodgson suggested a correlation between J and the Cu–O–Cu angle.[4,17–22] On the other hand in the literature only square-planar and square-pyramidal complexes were taken into account. The copper(II) complex is not isomorphous to the nickel(II) analogue, and ESR data are indicative of sensible distortions in the bonding environment of the copper(II) ion.[15,23] Therefore it appeared desirable for us to obtain X-ray structure information on the copper(II) complex, in order to discuss the magnetic coupling on the basis of the value of the bridging angle and the distortion of the five-coordinate environment around the copper(II) ions.

We wish to report here the results of this structural analysis together with new single-crystal ESR data on the zinc(II)-doped copper(II) complex, which allowed us to obtain some insight into the electronic structure of the dimers.

Experimental Section

The pure and zinc(II)-doped $Cu_2(bdhe)_2(ClO_4)_2$ derivatives were prepared as previously described.[15]

ESR spectra were obtained with the apparatus previously described.[24]

Collection and Reduction of X-ray Intensity Data. The deep green crystals of $[Cu_2(bdhe)_2](ClO_4)_2$ have a centrosymmetric shape, being surrounded by eight faces of the forms {011}, {0$\bar{1}$1}, {110}, and {$\bar{1}$10}. For the crystal chosen for X-ray collection, the distances between the pairs of these centrosymmetric faces are 0.25, 0.20, 0.35, and 0.35 mm, respectively. The unit cell is monoclinic, of space group $P2_1/n$, with $a = 9.349$ (2) Å, $b = 17.646$ (4) Å, $c = 11.720$ (3) Å, $\beta = 93.02$ (2)°, $V = 1934.07$ Å^3, d_{obsd} (by flotation) = 1.45 g cm^{-3}, $Z = 2$, mol wt 842.86, and $d_{calcd} = 1.447$ g cm^{-3}. Cell parameters were determined by carefully measuring the setting angles of 25 reflections at room temperature (22 °C), with Mo K_α monochromatized radiation by a flat graphite crystal ($\lambda = 0.709\,26$ Å), collected on a four-circle Philips PW 1100 automatic diffractometer.

The intensity data were also collected on this diffractometer with the same radiation. Data were collected with equatorial geometry with use of the θ–ω scan technique, with a takeoff angle of 3.0°. The scan of ω across the peak was equal to $0.8 \pm 0.69 \tan \omega$. The rate of collection was 0.08°/s; the background time was half of the peak time for each side. Three standard reflections were counted periodically every 120 min, but no systematic loss of intensity was observed during the automatic collection. The standard deviations on the intensity were calculated as reported elsewhere,[25] with a value for the instability factor K of 0.03. The 1367 reflections having $I > 3\sigma$ in the range $5° < 2\theta < 40°$, on a total of 1983 measured relfections, were considered observed and were used in the structure analysis. These reflections were corrected for absorption by a numerical method ($\mu = 12.58$ cm^{-1}); the transmission factor varied between 0.72 and 0.81. The intensities were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from the literature.[26] Corrections for anomalous dispersion effects were also applied.[26]

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis yielded the positional parameters of the copper atom. The other nonhydrogen atoms were located from successive three-dimensional F_o and ΔF Fourier maps. The oxygen atoms of the perchlorate ion are disposed in a distorted array, as was noticed by the electron density shown by the Fourier maps around the chlorine atom. This disorder was rationalized by considering three different arrangements of the four oxygen atoms around the chlorine atom which, on the contrary, appears to occupy only one position. The O_2 and O_3 atoms belong to two different models, and therefore their population parameter is $^2/_3$, whereas the other oxygens of the per-

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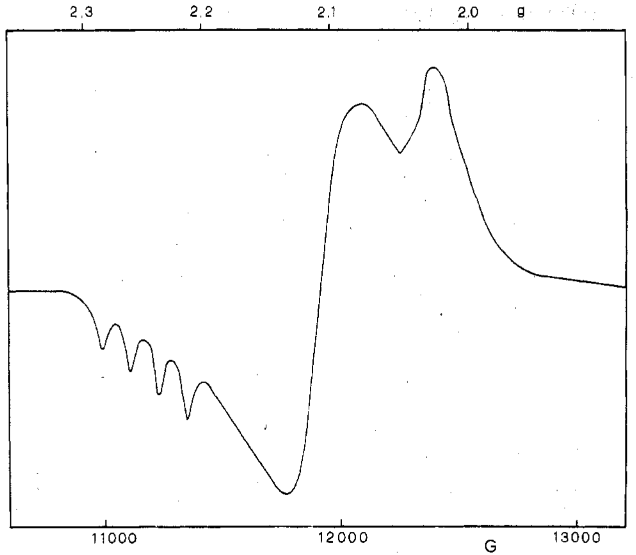

Figure 1. Polycrystalline powder ESR spectra (35 GHz) of zinc(II)-doped $[Cu_2(bdhe)_2](ClO_4)_2$.

chlorate ion have a population parameter of $^1/_3$.

The structure was refined by use of the full-matrix least-squares method of the SHELX program.[27] The minimized function is $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma(F_o)^2$. The hydrogen atoms were introduced in calculated positions, with an overall temperature factor U of 0.05 and were not refined. Their positions varied in every cycle on the basis of the shift of the carbon atoms (the C–H distance was fixed at 1.07 Å). Isotropic temperature factors were used for the carbon atoms, whereas anisotropic temperature factors were used for the other atoms. The final conventional R factor was 0.055, and the R_w factor, defined as $|\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2|^{1/2}$, was 0.056.

A refinement of the three ClO_4^- models as rigid groups was discarded since the R factor was sensibly higher (0.079), and also the temperature factors of some oxygen atoms reached very high values. A final ΔF Fourier synthesis did not show remarkable features, except for some residual diffuse electron density in the zone of the perchlorate ion. The final values of the parameters are reported in Tables I and II. Observed and calculated structure factors are available as supplementary material.

Results

ESR Data. The pure copper(II) complex does not give any detectable ESR signal, but useful information on the copper(II) environment can be gathered by adding low concentrations of zinc(II) to the reaction mixture, so that some ESR-active copper(II)–zinc(II) couples are formed in the essentially diamagnetic copper(II) lattice. The 9-GHz polycrystalline powder spectra were previously reported,[15] while the 35-GHz spectra are shown in Figure 1. The 35-GHz spectra can be better interpreted, yielding $g_1 = 2.25$, $g_2 = 2.12$, $g_3 = 2.03$, $A_1 = 120 \times 10^{-4}$ cm^{-1}, $A_2 < 30 \times 10^{-4}$ cm^{-1}, and $A_3 = 50 \times 10^{-4}$ cm^{-1}. In order to have information on the principal directions of the g and **A** tensors, we recorded also single-crystal spectra. They can be obtained at room temperature. On cooling to liquid nitrogen temperature the lines sharpen as expected, but the crystals show a large tendency to break. Many attempts were made by cooling the crystals very slowly, and some spectra could be recorded. In some instances these crystals also broke up after standing for a while at low temperature, so that these data could not be as accurate as we wished they could be.

Another complication in the analysis of the ESR data of the crystals lies in the fact that the prominent faces do not correspond to the principal planes of the unit cell. Three orthogonal rotations along the X, Y, and Z axes defined by the rotation matrix

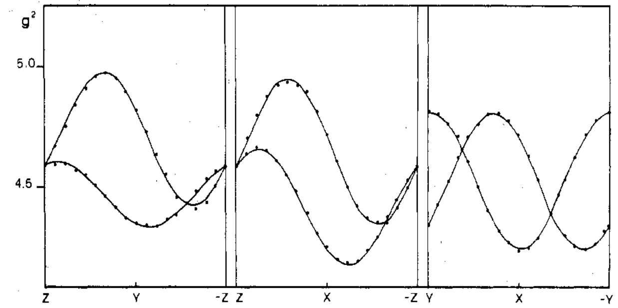

Figure 2. Angular dependence of the g^2 values in the three experimental rotations. X, Y, and Z are defined in the text.

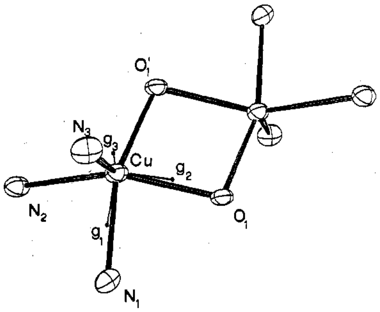

Figure 3. Orientation of the **g** tensor in the molecular frame.

Table III. Principal g Values and Directions for the Two Magnetically Nonequivalent $[Cu_2(bdhe)_2]^{2+}$ Cations in the Unit Cell[a]

g values	direction cosines		
Site 1			
$g_1 = 2.02$	0.8695	−0.1986	−0.4522
$g_2 = 2.12$	−0.4831	−0.5326	−0.6950
$g_3 = 2.25$	0.1029	−0.8227	0.5590
Site 2			
$g_1 = 2.02$	0.5205	−0.7290	−0.4445
$g_2 = 2.12$	0.3142	0.6477	−0.6941
$g_3 = 2.25$	0.7939	0.2217	0.5662

[a] Referred to the X, Y, and Z axes defined in the text.

$$\begin{pmatrix} 0.5527 & -0.8334 & 0 \\ 0.8334 & 0.5527 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

referred to the a, b, and c axes were performed, and the angular dependences of g^2 are given in Figure 2. The g^2 and A^2 tensors were calculated through a least-squares procedure. Diagonalization of the g^2 matrices corresponding to the two magnetically nonequivalent sites yielded the principal g values and directions shown in Table III. The two sets are within experimental error related by the symmetry elements of the $P2_1/n$ cell. The orientation of the **g** tensor within the molecular frame is shown in Figure 3.

Since the cell is monoclinic, this is not a unique choice. The other one, however, puts the principal axes of g away from any relevant bond directions, so that it is rejected. The g direction is close to the Cu–N(3) bond direction, making an angle of 13° with it, while the g_3 direction is relatively close to the Cu–O(1)′ and Cu–N(1) bond directions (15 and 5°, respectively).

The angular dependence of **A** is far less defined, owing to the overlap of the signals corresponding to the different sites and to the width of the signals. In the rotation around X there

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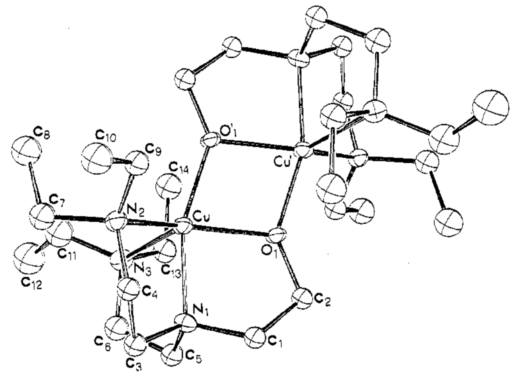

Figure 4. ORTEP drawing of the $[Cu_2(bdhe)_2]^{2+}$ cation.

Table IV. Interatomic Distances (Å), Angles (Deg), and Their Respective Standard Deviations

(A) Selected Bond Lengths

Cu···Cu′	3.044 (2)	C(3)–C(4)	1.511 (12)
Cu–O(1)	1.973 (5)	C(5)–C(6)	1.480 (12)
Cu–O(1)′	1.914 (6)	C(7)–C(8)	1.524 (14)
Cu–N(1)	1.993 (6)	C(9)–C(10)	1.530 (14)
Cu–N(2)	2.106 (6)	C(11)–C(12)	1.512 (16)
Cu–N(3)	2.504 (7)	C(13)–C(14)	1.512 (14)
N(1)–C(1)	1.494 (10)	Cl–O(2)	1.45 (2)
N(1)–C(3)	1.501 (10)	Cl–O(3)	1.47 (2)
N(1)–C(5)	1.507 (11)	Cl–O(4)	1.39 (6)
N(2)–C(4)	1.494 (10)	Cl–O(5)	1.35 (3)
N(2)–C(7)	1.500 (11)	Cl–O(6)	1.55 (3)
N(2)–C(9)	1.494 (11)	Cl–O(7)	1.27 (5)
N(3)–C(6)	1.484 (12)	Cl–O(8)	1.34 (17)
N(3)–C(11)	1.489 (12)	Cl–O(9)	1.27 (4)
N(3)–C(13)	1.499 (12)	Cl–O(10)	1.46 (3)
O(1)–C(2)	1.411 (9)	Cl–O(11)	1.26 (10)
C(1)–C(2)	1.528 (12)		

(B) Selected Bond Angles

Cu–O(1)–Cu′	103.1 (3)	Cu–O(1)–C(2)	115.4 (5)
O(1)–Cu–N(1)	84.0 (3)	Cu–N(1)–C(1)	104.9 (5)
O(1)–Cu–N(2)	138.5 (3)	Cu–N(1)–C(3)	108.6 (5)
O(1)–Cu–N(3)	109.5 (2)	Cu–N(1)–C(5)	111.3 (5)
O(1)–Cu–O(1)′	76.9 (2)	Cu–N(2)–C(4)	101.6 (5)
N(1)–Cu–N(2)	87.7 (3)	Cu–N(2)–C(7)	114.7 (5)
N(1)–Cu–N(3)	80.9 (3)	Cu–N(2)–C(9)	109.5 (5)
N(1)–Cu–O(1)′	160.6 (3)	Cu–N(3)–C(6)	98.7 (5)
N(2)–Cu–N(3)	109.1 (3)	Cu–N(3)–C(11)	120.3 (6)
N(2)–Cu–O(1)′	104.8 (3)	Cu–N(3)–C(13)	106.5 (5)
N(3)–Cu–O(1)′	108.0 (2)		

is some evidence of noncollinearity of **g** and **A**. The impossibility of obtaining good low-temperature data prevented us from analyzing further the hyperfine tensor.

Discussion

Description of the Structure. The structure consists of dinuclear $[Cu_2(bdhe)_2]^{2+}$ cations, which possess a center of symmetry (Figure 4), and of perchlorate anions. The copper(II) ions achieve five-coordination by sharing the oxygen atoms of the ligand. The Cu–O(1)–Cu′ angle is 103.1 (3)°. The donor set is therefore formed by three nitrogen and two oxygen atoms. The arrangement of the ligand around the metal ion does not conform either to a trigonal bipyramid or to a square pyramid. According to a trigonal-bipyramidal description the O(1), N(2), and N(3) atoms lie in the equatorial plane and O(1)′ and N(1), which is the central atom of the tripod ligand, in the axial positions. The copper(II) ion is 0.20 Å out of the equatorial plane, toward O(1)′. The copper(II)–copper(II) distance in the dimer is 3.044 (2) Å. Figure 5 shows a perspective view of the unit cell. Selected bond lengths and angles are listed in Table IV.

The three equatorial bond angles show a remarkable distortion from an idealized trigonal-bipyramidal geometry, since the angles N(2)–Cu–N(3), O(1)–Cu–N(3), and O(1)–Cu–N(2) assume values of 109.1 (3), 109.5 (2), and 138.5 (3)°, respectively. Moreover, the distance from the metal of the N(3) atom, which is opposite to the equatorial angle of 138.5°, is very long (2.504 (7) Å). This polyhedron can therefore be described as trigonal bipyramidal distorted toward square pyramidal with elongated axial distance, as usually has been found in square-pyramidal copper(II) complexes.[28]

If we compare this geometry with that found in the analogous complex of nickel(II),[16] $[Ni_2(bdhe)_2](ClO_4)_2$, we notice that this kind of distortion toward a square pyramid does not appear in the nickel(II) derivative, which has equatorial angles closer to those characteristic of a trigonal-bipyramidal geometry.

Structural investigations on other dinuclear five-coordinated copper(II) complexes having two oxygen-bridging atoms have been recently reported by Bertrand et al.[29,30] In the Cu(salPA)Cl complex[29] (salPA = (3-hydroxypropyl)salicylaldiminato) the copper(II) ions are in a distorted trigonal-bipyramidal arrangement, but the distortion from this idealized geometry is not toward a square pyramid. The Cu–O(1)–Cu′ angle in this complex is 110.3° and therefore significantly larger than that found in the title complex. In the bis(*N*-picolinoyl)(3-amino-1-propoxido)aquocopper(II)[30] the copper(II) ions are five-coordinated with two bridged oxygen atoms, but the coordination geometry is now better described as square pyramidal, with the oxygen atom of a water molecule in the axial position. The Cu–O–Cu′ angle is much smaller than that found in the title complex, i.e., 98.3°, and in the above-reported Cu(salPA)Cl complex.

Electronic Structure of the Dimer. The overall low symmetry of the complex shows up neatly also in the ESR spectra of the copper(II)–zinc(II) couple, through highly anisotropic g values. Similar values have been reported for other five-coordinated copper(II) complexes,[31-34] which have geometries intermediate between a square pyramid and a trigonal bipyramid. A simple model for rationalizing these data has been published previously,[31] which refers the g and A values of distorted five-coordinated complexes to one angular parameter. In the present case a different appropriate treatment seemed more appropriate, and we tried to reproduce the energies of the electronic transitions and the principal g values and directions through an angular overlap model that we have developed recently with some success.[35,36]

The electronic spectra of the pure copper(II) complex have been reported previously.[15] They show a maximum at 13 500 cm^{-1} with a shoulder at 10 000 cm^{-1}.

We attempted to reproduce these data by giving as an input to the computer the geometrical coordinates of the copper(II) and donor atoms seen in the crystal structure. Only the σ-bonding effects were taken into account. This seems to be a good assumption for the nitrogen donors, while it may be in fault for the oxygen donors. However, since too many parameters would be required, allowing for π interactions, we limited the calculation to the above assumptions. The five e_σ parameters for the five donor atoms were varied over a large

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Table V. Best Fit of Electronic Transitions and of the *g* Values and Directions[a]

transition energies, cm^{-1}		*g* values		direction cosines					
				calcd			obsd		
calcd	obsd	calcd	obsd						
9 380	10 000	$g_1 = 2.02$	$g_1 = 2.02$	0.9035	−0.1834	−0.3873	0.8695	−0.1986	−0.4522
11 040	13 500	$g_2 = 2.13$	$g_1 = 2.12$	−0.4182	−0.5743	−0.7038	−0.4831	−0.5326	−0.6950
12 950		$g_3 = 2.26$	$g_3 = 2.25$	0.0934	−0.7979	0.5956	0.1029	−0.8227	0.5590
14 100									

[a] AO parameters: $e_{\sigma(N_1)} = 5000$ cm^{-1}, $e_{\sigma(N_2)} = 4090$ cm^{-1}, $e_{\sigma(N_3)} = 1000$ cm^{-1}, $e_{\sigma(O_1)} = 5454$ cm^{-1}, $e_{\sigma(O_1')} = 6818$ cm^{-1}, $e_{\pi\sin} = e_{\pi\cos} = 0$ cm^{-1}, $k = 0.75$, $\zeta = 830.0$ cm^{-1}.

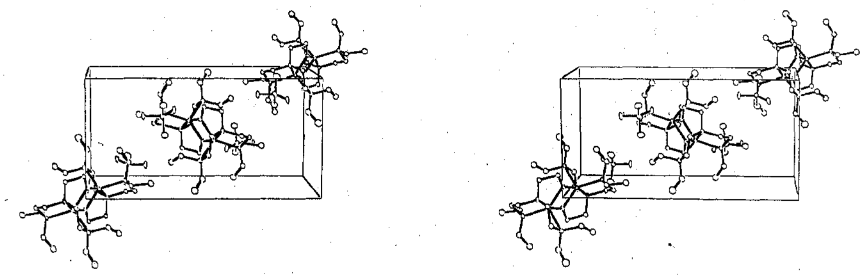

Figure 5. ORTEP view of the unit cell. The *a* axis is vertical, the *b* axis is horizontal, and the *c* axis points into the paper.

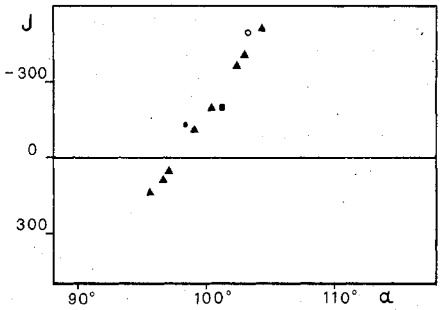

Figure 6. Dependence of *J* on the Cu–O–Cu angle in a series of dihydroxo-, dialkoxo-, and diphenoxo-bridged copper(II) dimers: ▲, ref 22; ■, ref 38; ●, ref 29; ○, present work.

range. Satisfactory agreement with the observed transitions was found by setting e_σ for N(3) to small values, in the range 300–1500 cm^{-1}, and the other four in the range 5000–7000 cm^{-1}. Also, the observed large anisotropy in the *g* value could be reproduced, together with the principal directions of the tensor. A representative fit is given in Table V. The values of the parameters shown in Table V were obtained from the tables published by Smith[37] and confirm the validity of the AO model in the fitting of the electronic properties of different complexes. It is remarkable that not only the *g* values were reproduced but also the principal directions, within 3°.

The above calculations confirm that the ligand field is intermediate between that of a trigonal bipyramid and of a square pyramid. Using the Cu–N(3) direction to locate the *z* molecular axis, one can describe the ground state as essentially $x^2 - y^2$ in nature, with some admixture of the other d orbitals.

Angular overlap calculations that we recently performed[11] showed that the values of *J* for couples of copper(II) ions should depend mainly on the nature of the bridging donor atoms and on the angle Cu–L–Cu, since the unpaired electrons can be considered to be in $x^2 - y^2$ orbitals. In the present case such a condition holds to a good approximation, and the bridging donors is an alkoxo group, which is sufficiently similar to the hydroxo group, so that a good correlation with the angular dependence of *J* previously reported[4] is anticipated.

The data available in the literautre for dihydroxo-, dialkoxo-, and diphenoxo-bridged dinuclear copper(II) complexes together with the present data are shown in Figure 6. It is apparent that the quasi linear relation still holds after the introduction of the new experimental points, although those of the alkoxo complexes tend to stay higher and that of the phenoxo complex is lower than the hydroxo points.

Acknowledgment. Thanks are expressed to Professor L. Sacconi for his constant encouragement.

Registry No. $[Cu_2(bdhe)_2](ClO_4)_2$, 73702-14-4.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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