of the ligands of $[L']^-$ they replace. The crystal field strength of the 3,2-Hopo ligand is expected to increase upon N-deprotonation due to the increased negative charge on the ligand, and indeed, blue shifts are observed upon successive deprotonations of FeL_3. However, deprotonation is also expected to raise the ligand orbital energies, and this offsetting effect may account for the small size of the observed blue shift.

Summary. A general and efficient synthetic route to *N*-alkyl-3-hydroxy-2(1*H*)-pyridinone ligands has been devised. The solid-state and neutral and acidic pH solution chemistry of these ligands is similar to that of the N-unsubstituted ligand, 3,2-Hopo. However, in basic solution, the complexes of 3,2-Hopo derive added stability by deprotonating at the ring nitrogen of each ligand, an option unavailable to the N-substituted molecules such as FeL'_3.

Acknowledgment. Walter Kwan assisted with the development of some of the synthetic methods described in this paper. Dr. Larry Loomis helped design and program the automatic spectrophotometric titrator. The crystal structures were performed at the CHEXRAY Diffraction Facility (supported in part by grants from the National Science Foundation), directed by Dr. Fred Hollander. This research was supported by NIH Grant AM32999.

Registry No. **1**, 39658-49-6; **2**, 116407-51-3; **3**, 116407-52-4; **4**, 116407-53-5; 3,2-Hopo, 16867-04-2; 2,5-dimethoxy-2,5-dihydrofuran-2-carboxylic acid methyl ester, 62435-72-7; *n*-butylamine, 109-73-9.

Supplementary Material Available: Tables S1 and S4 (general temperature factor expressions for **3** and **4**), Table S2 (fixed positional parameters and thermal parameters for hydrogen atoms in **3**), Table S5 (fixed positional and thermal parameters and occupancy factors for hydrogen atoms in **4**), Figure S1 (orthogonal component spectra for titrations of ferric ion with HL′), Figure S2 (results from least-squares fit to data of spectral titrations of Fe^{3+} and HL′), Figure S3 (orthogonal component spectra for titrations of Fe^{3+} and L), and Figure S4 (results from least-squares fits to spectral data from titrations of ferric ion with HL) (8 pages); Tables S3 and S6 (observed and calculated structure factors for **3** and **4**) (23 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica and Dipartimento di Scienza della Terra,
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Out-of-Plane Coordination and Exchange Coupling in Oxygen-Bridged Copper(II) Dimers[1]

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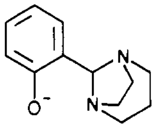
The syntheses, crystal and molecular structures, and magnetic properties are reported for the new compounds $Cu_2L_2(CH_3COO)_2\cdot 2C_2H_5OH$ (compound E) and $Cu_2L_2(CH_3COO)_2\cdot 2CH_3OH$ (compound M), where L^- is the ligand

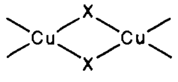


Compounds E and M, which are isostructural, crystallize in the monolinic space group $P2_1/a$, $Z = 2$. Cell dimensions are as follows. Compound E ($Cu_2C_{32}H_{48}N_4O_8$): $a = 20.867$ (3), $b = 10.168$ (3), $c = 7.960$ (3) Å; $\beta = 94.12$ (2)°. Compound M ($Cu_2C_{30}H_{44}N_4O_8$): $a = 20.627$ (3), $b = 9.987$ (3), $c = 7.839$ (3) Å; $\beta = 92.41$ (2)°. The structures were solved by Patterson and Fourier methods and refined to an *R*(unweighted) value of 0.047 for E and 0.041 for M. The two complexes consist of centrosymmetric dimeric units that are well separated from one another. The binuclear structures are held together by phenoxo bridges between the copper atoms. The Cu–O(bridging) separations average 1.97 Å. The bridging CuOCu angles in E and M are 101.6 (4) and 102.4 (1)°, respectively. The geometry around the copper atoms may be described as distorted square-pyramidal. The apical, weak bond involves the oxygen atom of the solvent molecule and is stronger in E, 2.267 (4) Å, than in M, 2.370 (4) Å. The base of the coordination pyramid deviates from planarity, and the distortion may be approximately described as being toward tetrahedral geometry. The dihedral angle, τ, between the bridging plane and the plane of the remaining ligands is 14° in both compounds. The two dimers exhibit antiferromagnetic exchange interactions with singlet–triplet splittings of 364 cm^{-1} for E and 420 cm^{-1} for M. A comparison of the structural and magnetic data obtained for the present compounds with corresponding data for previously characterized planar and nonpolar compounds involving similarly bridged Cu_2O_2 moieties indicates that the apical ligands have a definite role in the magnetic coupling in E and M. A general discussion of the magnetic consequences that may be expected when the coordination environment at copper changes from 4 to (4 + 1) is also given.

Introduction

Doubly bridged copper(II) dimers involving a Cu_2O_2 moiety, owing to the rather unique variety of structural types and spin–spin interactions that characterize their crystal chemistry, have provided a rich opportunity for the investigation of structural effects on magnetic coupling.[2]

Hatfield et al.[2a,b,3] have demonstrated that, in planar hydroxo-bridged dimers of type I, the singlet–triplet splitting resulting from exchange coupling, $-2J$, is a linear function of the bridging CuOCu angle, ϕ, according to eq 1. A quite different structural dependence of the magnetic properties has been observed by Sinn et al.[4] for a series of diphenoxo-bridged dimers of type II, in which the ligand environment is considerably distorted from planar toward tetrahedral geometry. These compounds conform to eq 2,[1c] where τ is the dihedral angle between the plane of the Cu_2O_2 bridging unit and the plane of the remaining ligands, III.



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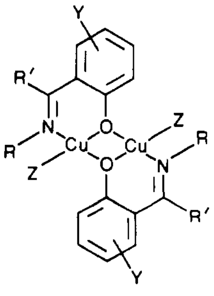
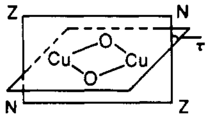


II



III

$$2J\ (cm^{-1}) = -74.53\phi + 7270 \qquad (1)$$

$$2J\ (cm^{-1}) = 29.7\tau - 1473 \qquad (2)$$

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Another interesting and not yet well-understood difference between the magnetic behaviors of compounds of type I and type II is suggested by the magnetic consequences of changing the copper coordination geometry from 4 to (4 + 1). While the additional coordination does not have any discernible influence on the magnetic properties of those type I compounds which obey eq 1 (these dimers exhibit either planar or tetragonal-pyramidal copper environments),[2a,b] the only characterized example of a type II compound having (4 + 1) distorted square-pyramidal geometry at copper, namely $[Cu(etsal)NO_3]_2$, seriously deviates from the correlation between magnetism and tetrahedral distortion, seemingly as a reflection of the different structure.[1c,5] Recent work from this laboratory[1c] has allowed us to rationalize (with use of semiempirical MO theory[6]) the relative merit of ϕ and/or τ in determining $-2J$ for compounds of type I and type II. With an aim toward obtaining some further understanding of the effect of a weak, apical coordination on magnetic coupling in nonplanar, oxygen-bridged copper(II) dimers of type II, we now describe the syntheses and the structural and magnetic properties of two new compounds: $Cu_2L_2(CH_3COO)_2{\cdot}2C_2H_5OH$ (compound E) and $Cu_2L_2(CH_3COO)_2{\cdot}2CH_3OH$ (compound M), where L^- indicates a new ligand deriving from the condensation of 1,4-diazacycloheptane with salicylaldehyde.

Experimental Section

Syntheses. LH. 1,4-Diazacycloheptane (3.00 g, 0.03 mol) was added to a 3.66-g (0.03-mol) quantity of salicylaldehyde. The addition was made over a period of 30 min, with constant stirring and under a dry nitrogen atmosphere. The reaction turned out to be strongly exothermic. The final mixture was allowed to cool to room temperature. After the mixture was allowed to stand about 4 h at room temperature, the white solid that formed was decanted and then dissolved in absolute ethanol (15 mL). A clear solution was obtained. To this solution was water added dropwise, with stirring, until the solution became slightly turbid. After the mixture was allowed to stand about 12 h at room temperature, a white, crystalline precipitate of the new LH ligand was collected by filtration, washed with the minimum amount of absolute ethanol, and dried under vacuum: yield 3.78 g (61.7%); mp 104–106 °C. Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.71; H, 7.93; N, 13.67. The compound can be recrystallized, in a very low yield, from absolute ethanol.

Compound E. A 1.00-g (5-mmol) quantity of $Cu(CH_3COO)_2{\cdot}H_2O$ was added to a solution of LH (1.02 g, 5 mmol) in absolute ethanol (100 mL). The addition was made over a period of 10 min, at 50 °C, with constant stirring. The warm, dark green solution was then filtered, and the filtrate was allowed to stand at room temperature for 24 h. A dark green, crystalline material separated, which was collected by filtration and dried under vacuum: yield 1.4 g (76%); mp 150–152 °C. Anal. Calcd for $C_{32}H_{48}N_4O_8Cu_2$: C, 51.63; H, 6.58; N, 7.53. Found: C, 51.45; H, 6.61; N, 7.47.

Compound M. This dark green compound was prepared by the above procedure for the synthesis of E, except for the use of absolute methanol (instead of absolute ethanol) as solvent and the use of a slightly higher ligand to metal ratio of 1.3. The slight ligand excess was used to avoid contamination of crystalline M by coprecipitation of copper acetate. Yield: 70%, based on original copper. Mp: 165–168 °C. Anal. Calcd for $C_{30}H_{44}N_4O_8Cu_2$: C, 50.34; H, 6.20; N, 7.83. Found: C, 50.21; H, 6.15; N, 7.72.

The two new compounds are stable in inert atmosphere. Although a slow decomposition occurs upon exposure to air, the decomposition process takes about 1 month to become perceptible.

Magnetic Measurements. ESR spectra and variable-temperature magnetic susceptibility data were collected as previously described.[7] Susceptibilities were corrected for the diamagnetism of the ligand system (-177.1×10^{-6} cgsu/Cu atom for E and -170.9×10^{-6} cgsu/Cu atom for M) and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

X-ray Data and Structure Solution. Compound M. A dark green tabular crystal with dimensions $0.39 \times 0.24 \times 0.15$ mm^3 was mounted on a computer-controlled Philips PW 1100 single-crystal diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The crystals are monoclinic. The cell dimensions, determined by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 17 and 25°, are as follows: $a = 20.627$ (3), $b = 9.987$ (3), $c = 7.839$ (3) Å; $\beta = 92.41$ (2)°; V = 1613.4 Å^3. The space group is $P2_1/a$ (from systematic extinctions). The calculated density for two dimeric molecules ($Cu_2C_{30}H_{44}N_4O_8$, $M_r = 716$) in the unit cell is 1.473 g·cm^{-3}. The absorption coefficient for Mo Kα is $\mu = 13.5$ cm^{-1}. The intensities were collected at room temperature up to $2\theta = 50°$. The ω–2θ scan technique was employed, the scan range being 1.5° and the speed 0.05° s^{-1}. A total of 3150 independent reflections were measured, of which 1068, having $I < 3\sigma(I)$, were considered as "unobserved" and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North et al;[8] the transmission factors were in the range 0.95–0.75.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares method with use of the SHELX-76 package of programs.[9] The quantity minimized was $(|F_o| - |F_c|)^2$. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms (with the exception of those of the methyl groups) were included at the calculated positions (C–H = 1.08 Å) with overall isotropic parameter, U, which refined to the value of 0.05 Å^2. The methyl groups were refined as rigid groups starting from the staggered positions. The common U of the hydrogen atoms of the methyl groups refined to 0.17 Å^2. The refinement converged at R(unweighted) = 0.041 and R(weighted) = 0.046 ($w = (\sigma^2(F_o) + 0.0006F_o^2)^{-1}$) for 208 parameters and 2082 observed reflections.

Compound E. A dark green tabular crystal with dimensions $0.25 \times 0.15 \times 0.10$ mm^3 was mounted on the diffractometer and treated with the same procedure as that described for compound M. The crystals are monoclinic, space group $P2_1/a$ (from systematic extinctions). Lattice parameters: $a = 20.867$ (3), $b = 10.168$ (3), $c = 7.960$ (3) Å; $\beta = 94.19$ (2)°; $V = 1684.4$ Å^3. The calculated density for two dimeric molecules ($Cu_2C_{32}H_{48}N_4O_8$, $M_r = 744$) in the unit cell is 1.446 g·cm^{-3}. The absorption coefficient is $\mu = 12.9$ cm^{-1}. A total of 3170 independent intensity data were measured in the 2θ range 4–50°, with the same technique and collection parameters as those for compound M. There were 1002 reflections with $I < 3\sigma(I)$ that were considered as "unobserved". The data were corrected for geometrical and physical factors as in the case of compound M. Transmission factors were in the range 0.96–0.77.

As inferred from a comparison between the symmetry and the lattice parameters, compounds E and M are isostructural. Therefore, the structure of E was refined by using, initially, the atomic coordinates of M and the same procedures. After some refinement cycles, the additional carbon atom in the asymmetric unit was located on the basis of a difference Fourier synthesis. Anisotropic thermal parameters were assigned to Cu, O, N, and C atoms. The overall temperature factor of phenylic or methylenic H atoms refined to 0.06 Å^2. The final R index was 0.047 for 2168 observations and 217 parameters ($R_w = 0.052$, $w = (\sigma^2(F_o) + 0.0042F_o^2)^{-1}$). The atomic scattering factors were taken from ref 9 for O, N, C, and H and from ref 10 for Cu; the correction for anomalous dispersion was included.

Results

Description of the Structures. The isostructural E and M compounds consist of neutral, well-separated dimeric units. The

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Table I. Fractional Atomic Coordinates in Compound M

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.06403 (2)	−0.07010 (5)	−0.03545 (7)
O(1)	0.0307 (1)	0.0813 (3)	0.0892 (4)
O(2)	0.0881 (2)	−0.2313 (3)	−0.1546 (4)
O(3)	0.0933 (2)	0.0673 (4)	−0.2664 (5)
O(4)	0.0841 (3)	−0.1619 (5)	−0.4215 (6)
N(1)	0.1474 (2)	−0.0721 (3)	0.1086 (5)
N(2)	0.2228 (2)	0.0259 (4)	0.3014 (5)
C(1)	0.0701 (2)	0.1882 (4)	0.1220 (5)
C(2)	0.0501 (2)	0.3171 (5)	0.0913 (7)
C(3)	0.0896 (3)	0.4271 (5)	0.1195 (8)
C(4)	0.1490 (3)	0.4069 (4)	0.2008 (7)
C(5)	0.1706 (2)	0.2792 (4)	0.2389 (6)
C(6)	0.1318 (2)	0.1680 (4)	0.1985 (5)
C(7)	0.1541 (2)	0.0294 (4)	0.2535 (6)
C(8)	0.2361 (3)	−0.0989 (5)	0.3945 (7)
C(9)	0.2198 (3)	−0.2257 (5)	0.2901 (7)
C(10)	0.1546 (2)	−0.2084 (4)	0.1903 (6)
C(11)	0.2047 (2)	−0.0386 (5)	0.0046 (6)
C(12)	0.2544 (2)	0.0238 (5)	0.1372 (7)
C(13)	0.0865 (3)	−0.2492 (5)	−0.3138 (7)
C(14)	0.0844 (4)	−0.3948 (6)	−0.3717 (9)
C(15)	0.0599 (5)	0.1771 (9)	−0.3397 (10)

Table II. Bond Distances (Å) and Angles (deg) in Compound M

Cu–O(1)	1.942 (3)	N(1)–C(11)	1.502 (6)
Cu–O(1)′	1.985 (2)	N(2)–C(7)	1.451 (6)
Cu–O(2)	1.936 (3)	N(2)–C(8)	1.464 (7)
Cu–O(3)	2.370 (4)	N(2)–C(12)	1.467 (6)
Cu–N(1)	2.017 (4)	C(6)–C(7)	1.516 (6)
O(1)–C(1)	1.360 (5)	C(8)–C(9)	1.537 (7)
O(2)–C(13)	1.260 (6)	C(9)–C(10)	1.537 (7)
O(3)–C(15)	1.405 (10)	C(11)–C(12)	1.559 (7)
O(4)–C(13)	1.213 (7)	C(13)–C(14)	1.523 (8)
N(1)–C(7)	1.524 (6)	Cu···Cu′	3.061 (1)
N(1)–C(10)	1.509 (5)		
O(1)–Cu–O(2)	173.5 (1)	C(10)–N(1)–C(11)	111.5 (3)
O(1)–Cu–O(3)	92.3 (1)	C(7)–N(2)–C(8)	108.1 (4)
O(1)–Cu–N(1)	92.2 (1)	C(7)–N(2)–C(12)	103.8 (3)
O(1)–Cu–O(1)′	77.6 (1)	C(8)–N(2)–C(12)	110.2 (4)
O(2)–Cu–O(3)	92.0 (2)	O(1)–C(1)–C(2)	121.1 (3)
O(2)–Cu–N(1)	91.8 (2)	O(1)–C(1)–C(6)	119.6 (3)
O(2)–Cu–O(1)′	96.9 (1)	C(1)–C(6)–C(7)	120.9 (3)
O(3)–Cu–N(1)	101.2 (1)	C(5)–C(6)–C(7)	119.8 (3)
O(3)–Cu–O(1)′	98.7 (1)	N(1)–C(7)–N(2)	103.5 (3)
N(1)–Cu–O(1)′	157.9 (1)	N(1)–C(7)–C(6)	112.2 (3)
Cu–O(1)–C(1)	119.0 (2)	N(2)–C(7)–C(6)	112.2 (3)
Cu–O(1)–Cu′	102.4 (1)	N(2)–C(8)—C(9)	113.8 (5)
C(1)–O(1)–Cu′	131.3 (2)	C(8)–C(9)–C(10)	110.2 (5)
Cu–O(2)–C(13)	126.8 (4)	N(1)–C(10)–C(9)	112.7 (4)
Cu–O(3)–C(15)	128.9 (5)	N(1)–C(11)–C(12)	103.7 (3)
Cu–N(1)–C(7)	117.3 (3)	N(2)–C(12)–C(11)	106.6 (3)
Cu–N(1)–C(10)	108.2 (3)	O(2)–C(13)–O(4)	125.9 (6)
Cu–N(1)–C(11)	111.5 (3)	O(2)–C(13)–C(14)	115.5 (5)
C(7)–N(1)–C(10)	106.2 (3)	O(4)–C(13)–C(14)	118.6 (6)
C(7)–N(1)–C(11)	102.0 (3)		

Table III. Fractional Atomic Coordinates in Compound E

atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.06254 (2)	−0.06867 (5)	−0.03579 (6)
O(1)	0.0317 (1)	0.0797 (3)	0.0908 (4)
O(2)	0.0850 (2)	−0.2272 (3)	−0.1526 (4)
O(3)	0.0882 (2)	0.0625 (4)	−0.2512 (5)
O(4)	0.0989 (3)	−0.1563 (5)	−0.4112 (5)
N(1)	0.1464 (2)	−0.0740 (3)	0.1085 (4)
N(2)	0.2239 (2)	0.0224 (4)	0.2956 (5)
C(1)	0.0711 (2)	0.1850 (4)	0.1203 (5)
C(2)	0.0505 (2)	0.3117 (4)	0.0794 (6)
C(3)	0.0906 (3)	0.4189 (4)	0.1156 (8)
C(4)	0.1514 (2)	0.4002 (4)	0.1884 (7)
C(5)	0.1731 (2)	0.2735 (4)	0.2250 (6)
C(6)	0.1333 (2)	0.1649 (4)	0.1903 (5)
C(7)	0.1554 (2)	0.0284 (4)	0.2474 (5)
C(8)	0.2374 (3)	−0.1000 (5)	0.3935 (7)
C(9)	0.2180 (3)	−0.2234 (5)	0.2923 (7)
C(10)	0.1533 (2)	−0.2047 (5)	0.1937 (6)
C(11)	0.2022 (2)	−0.0460 (5)	0.0082 (6)
C(12)	0.2531 (2)	0.0158 (5)	0.1335 (6)
C(13)	0.0931 (2)	−0.2443 (5)	−0.3060 (7)
C(14)	0.0949 (4)	−0.3869 (6)	−0.3636 (8)
C(15)	0.0435 (4)	0.1536 (9)	−0.3353 (11)
C(16)	0.0750 (7)	0.2645 (9)	−0.3954 (13)

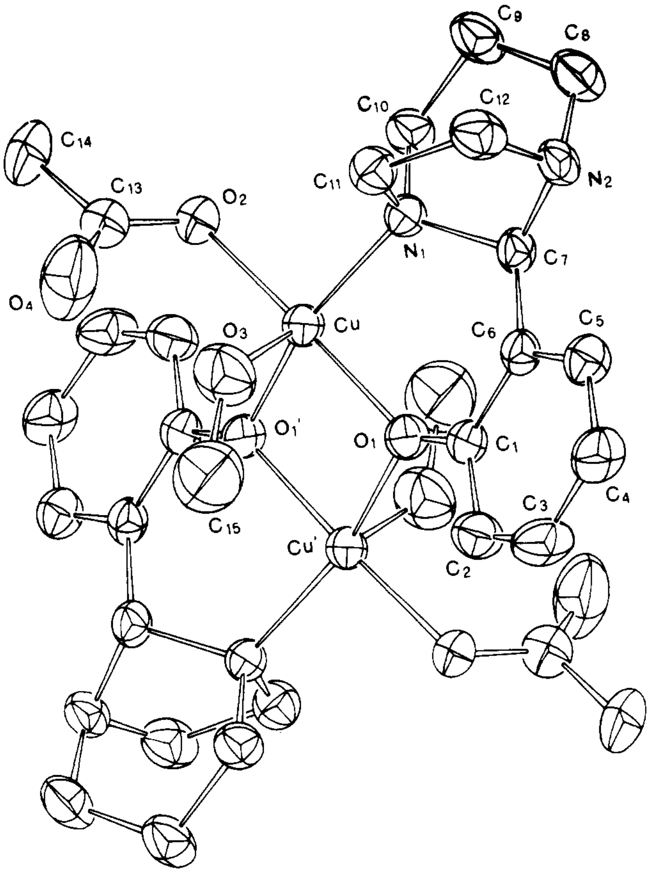

Figure 1. View of the molecular structure of the binuclear units in compound M. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

dimeric units are centrosymmetric. Final positional parameters and the more important interatomic distances and bond angles are given in Tables I–IV. The structure of M is presented in Figure 1. The two copper atoms are doubly bridged by phenoxide groups. The two Cu_2O_2 moieties are exactly planar owing to crystallographic inversion symmetry. The Cu–O(bridging) separations average 1.97 Å in both compounds. This value compares well with corresponding values (in the range 1.93–1.96 Å) in the compounds of type II whose structures have so far been determined.[1c,5,11-14] Also, the phenolic C(1)–O(1) bond distance of 1.360 (5) Å (in both compounds) is normal for compounds of type II. The bridging angle at oxygen (102.4 (1)°) and consequently the Cu···Cu′ separation (3.061 (1) Å) in M differ little from the corresponding parameters in E, 101.6 (1)° and 3.050 (1) Å, respectively. Besides the two bridging phenolic oxygens, the coordination sphere of the copper atoms contains one nitrogen of 1,4-diazacycloheptane, one oxygen of an acetate anion, and the oxygen atom of the solvent molecule. The second oxygen atom

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Table IV. Bond Distances (Å) and Angles (deg) in Compound E

Cu-O(1)	1.949 (3)	N(1)-C(11)	1.487 (6)
Cu-O(1)′	1.986 (2)	N(2)-C(7)	1.454 (5)
Cu-O(2)	1.936 (3)	N(2)-C(8)	1.484 (7)
Cu-O(3)	2.267 (4)	N(2)-C(12)	1.468 (6)
Cu-N(1)	2.023 (4)	C(8)-C(9)	1.530 (7)
O(1)-C(1)	1.360 (5)	C(9)-C(10)	1.523 (7)
O(2)-C(13)	1.257 (6)	C(11)-C(12)	1.537 (6)
O(3)-C(15)	1.444 (9)	C(13)-C(14)	1.522 (8)
O(4)-C(13)	1.237 (7)	C(15)-C(16)	1.407 (14)
N(1)-C(7)	1.520 (5)	Cu···Cu′	3.050 (1)
N(1)-C(10)	1.494 (6)		
O(1)-Cu-O(2)	173.5 (1)	C(10)-N(1)-C(11)	111.2 (3)
O(1)-Cu-O(3)	92.3 (1)	C(7)-N(2)-C(8)	108.6 (4)
O(1)-Cu-N(1)	91.8 (1)	C(7)-N(2)-C(12)	103.5 (3)
O(1)-Cu-O(1)′	78.4 (1)	C(8)-N(2)-C(12)	110.4 (4)
O(2)-Cu-O(3)	92.7 (2)	O(1)-C(1)-C(2)	121.1 (3)
O(2)-Cu-N(1)	91.2 (2)	O(1)-C(1)-C(6)	119.3 (3)
O(2)-Cu-O(1)′	96.8 (1)	C(1)-C(6)-C(7)	120.5 (3)
O(3)-Cu-N(1)	101.7 (1)	C(5)-C(6)-C(7)	119.9 (3)
O(3)-Cu-O(1)′	98.7 (1)	N(1)-C(7)-N(2)	103.3 (3)
N(1)-Cu-O(1)′	157.7 (1)	N(1)-C(7)-C(6)	112.9 (3)
Cu-O(1)-C(1)	118.7 (2)	N(2)-C(7)-C(6)	112.8 (3)
Cu-O(1)-Cu′	101.6 (1)	N(2)-C(8)-C(9)	112.2 (5)
C(1)-O(1)-Cu′	131.2 (2)	C(8)-C(9)-C(10)	111.1 (4)
Cu-O(2)-C(13)	129.5 (3)	N(1)-C(10)-C(9)	113.4 (4)
Cu-O(3)-C(15)	123.2 (4)	N(1)-C(11)-C(12)	105.1 (3)
Cu-N(1)-C(7)	116.8 (3)	N(2)-C(12)-C(11)	106.1 (3)
Cu-N(1)-C(10)	109.4 (3)	O(2)-C(13)-O(4)	125.7 (5)
Cu-N(1)C(11)	111.7 (3)	O(2)-C(13)-C(14)	115.6 (4)
C(7)-N(1)-C(10)	106.0 (3)	O(4)-C(13)-C(14)	118.6 (5)
C(7)-N(1)-C(11)	101.5 (3)	O(3)-C(15)-C(16)	111.7 (8)

of each carboxylate ligand and the second nitrogen atom of 1,4-diazacycloheptane are not involved in any bonding. The geometry around the copper atoms may be described as distorted (4 + 1) square-pyramidal. The apical bond involves the oxygen atom of the solvent molecule and is weaker than the other four bonds by about 0.2–0.3 Å. The Cu–N(1) distances in the two compounds (2.017 (4) and 2.023 (4) Å) agree with values reported in the literature for tertiary amine–Cu(II) bond lengths.[7,12,15]

The apical Cu–O(3) bond length is significantly longer in M (2.370 (4) Å) than in E (2.267 (4) Å). The base of the coordination pyramid deviates from planarity, and the distortion may approximately be described as being toward tetrahedral geometry. The dihedral angle, τ, between the planes CuO(1)Cu′O(1)′ and CuN(1)O(2)Cu′N(1)′O(2)′ is 14.0° in both compounds. The angle formed by the apical bond with the best basal plane is 88° in M and 86° in E. The 1,4-diazacycloheptane ring is in a chair-shaped conformation.

In conclusion, the present compounds are similar in structure to the characterized compounds of type II except for the presence of the apical bonds. In addition, the most significant structural difference between the two compounds is the longer axial bond in M than in E.

Magnetic Measurements. Corrected magnetic susceptibility data for E and M, in the range from 90 to 300 K, are given in Figures 2 and 3, respectively. For both compounds, the slope of the χ_M vs T curve changes abruptly at about 310–320 K. This feature is interpreted as being indicative of some decomposition process, probably connected to a loss of solvent molecules. Data above 300 K were, therefore, not considered in the fitting process. The usual dipolar coupling approach of Van Vleck, with a perturbing Hamiltonian $-2J(\hat{S}_A \cdot \hat{S}_B)$ and $S_A = S_B = {}^1/_2$, was used to fit the experimental susceptibility data. The magnetic susceptibility expression was

$$\chi_M/\mathrm{Cu} = \frac{Ng^2\mu_B^2}{3kT}\left(1 + \frac{1}{3}X^2\right)^{-1} + N\alpha \tag{3}$$

where $X = \exp(-J/kT)$ and the other symbols have their usual meanings. The function that was minimized in curve fitting, with use of a nonlinear fitting routine, was $F = \sum(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2 \cdot (\chi_i^{\text{obsd}})^{-1}$. For M, the best fit to the data yielded $J = -210 \pm 3$ cm^{-1}, $g = 2.15 \pm 0.01$, and $F = 5 \times 10^{-6}$ (for 44 observations); for E, $J = -182 \pm 3$ cm^{-1}, $g = 2.15 \pm 0.01$, and $F = 6 \times 10^{-6}$ (for 45 observations). For both M and E, the analysis of the susceptibility data did not indicate the presence of any significant amount of magnetically dilute cupric impurities.

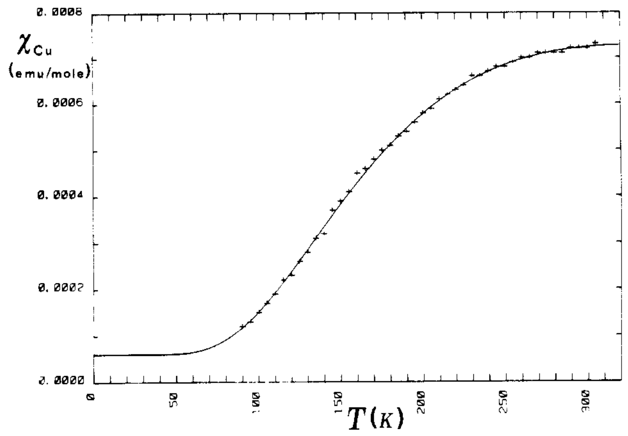

Figure 2. Magnetic susceptibility data for compound E. The best fit described in the text is shown as the full line.

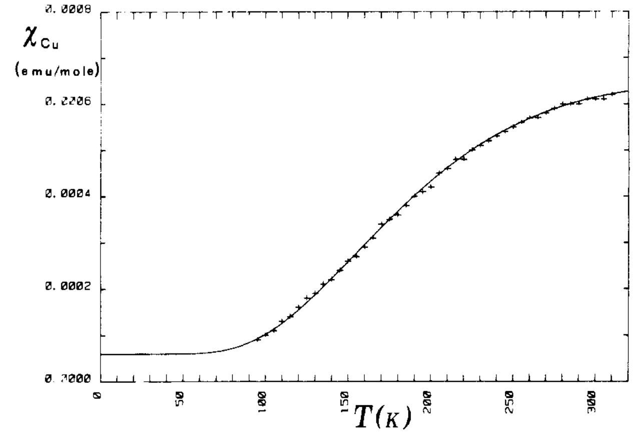

Figure 3. Magnetic susceptibility data for compound M, along with the fit described in the text.

The X-band ESR spectra of powdered samples of each compound, at both 77 and 300 K, showed four lines with a hyperfine splitting of about 150 G. Several superhyperfine patterns were also discernible. Glasses of solutions in CH_2Cl_2 gave the same features as the polycrystalline samples. The observed spectral behavior is typical of magnetically dilute Cu(II) compounds and is attributable to the presence of noncoupled impurities that are not revealed by the magnetic susceptibility data. The observation of the hyperfine and superhyperfine splittings in the powder spectra indicates that the noncoupled species are diluted in an essentially diamagnetic host lattice. It is concluded that the pure dimeric complexes do not give any detectable ESR signal.

Discussion

The molecular structures of the present dimers are closely related to those of the characterized compounds of type II except for the small τ angle of 14.0° and the additional, weak, axial coordination to copper.

Magnetically, E and M exhibit singlet–triplet splittings of 364 and 420 cm^{-1}, respectively. These values are (i) not in agreement with eq 2, as expected[1c] on the basis of the small (but not negligible) τ angle, (ii) midway in the range 300–500 cm^{-1} (corresponding to a range of τ values from 33 to 40°), observed for those type II compounds which obey the correlation between magnetism and tetrahedral distortion,[1c] and (iii) considerably smaller than the values (in the range 600–700 cm^{-1}) found[16-19] for virtually

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planar ($\tau \sim 0°$) diphenoxo-bridged dimers with ϕ angles in the range 100–105°, i.e. reasonably similar to those observed in E and M (although no clear dependence of $2J$ upon ϕ has been reported so far for planar diphenoxo-bridged dimers, a trend similar to that observed with the hydroxo-bridged systems may be reasonably expected).[6,16,19,20]

For the purpose of the present discussion, two main conclusions can be drawn from these data: (i) The E and M singlet–triplet splittings cannot be reasonably explained in terms of the τ and/or ϕ structural parameters, without taking into account the axial ligands. (ii) The presence of the additional, axial bond reduces the singlet–triplet splitting. It is pertinent to note that similar concepts have been proposed by Sinn[5] concerning the structural dependence of the magnetic properties of $[Cu(etsal)NO_3]_2$ (etsal = ethylsalicylaldimine), the only characterized example of a type II compound with distorted (4 + 1) square-pyramidal geometry at copper that has so far been reported. This etsal derivative shows an apical Cu–O bond length of 2.448 (3) Å, $\phi = 101\ (1)°$, $\tau = 27.4°$, and $-2J = 166$ cm^{-1}.

The relative magnetic coupling in E and M further witnesses the role of the axial bonds in magnetic exchange. As mentioned above, the X-ray structures of the two dimers are virtually identical in all respects except for the shorter axial bond length in E, 2.267 (4) Å, than in M, 2.370 (4) Å. The weaker antiferromagnetic interaction in E than in M is, therefore, indicative that the singlet–triplet splitting decreases as the axial bond strength increases. The fact that $[Cu(etsal)NO_3]_2$, relative to E and M, exhibits a longer apical Cu–O bond length and a smaller singlet–triplet splitting cannot be taken as evidence in contrast with this concept, for the etsal compound shows a substantially larger twist angle (vide infra).

Symmetry considerations are useful to account for the combined effect of the τ angle and the fifth ligand on magnetic coupling and to deal with the closely related problem of why the superexchange interaction in systems of type II is much more sensitive to the presence of an additional, apical bond than the interaction in e.g. the virtually planar hydroxo-bridged systems of type I, in which there is no perturbing influence from such bonds.

According to current orbital models for superexchange,[6,21–23] the extent of antiferromagnetic coupling in a bridged copper(II) dimer is mainly related to the "superexchange overlap" along the bridging bonds. The larger the overlap, the stronger the antiferromagnetic interaction. Since all of the systems under discussion involve a planar Cu_2O_2 framework, the superexchange overlap depends on the orientation of the copper unpaired-electron orbital relative to the bridging plane (the xy plane). In other words, the antiferromagnetic interaction is expected to become weaker as the copper unpaired electron density in the bridging plane diminishes.

For a planar system of type I, the site symmetry at copper is very nearly C_{2v} and the unpaired electron is described by an almost pure orbital of b_2 symmetry, d_{xy}, pointing directly at the bridge atoms. There is no out-of-plane unpaired electron density and, in qualitative agreement with eq 1, the overlap depends on the ϕ angle. A τ distortion reduces the site symmetry from C_{2v} to C_2. In this latter symmetry d_{xy} and d_{xz} belong to the same b irreducible representation and the d_{xy} orbital incorporates d_{xz} character to lie in the plane midway between the xy plane and the plane containing the copper and the nonbridging donor atoms. As the τ angle increases, the in-plane unpaired-electron density decreases, which qualitatively justifies eq 2. The addition of a weak apical bond further reduces the site symmetry at copper, from C_2 to C_1. The formerly pure d_{xy} orbital can now mix not only with d_{xz} but also with d_{z^2}, owing to the common a symmetry. A stronger axial bond obviously increases the importance of the component along the z axis, thus decreasing the in-plane electron density at copper. This concept is in agreement with the relative magnetic coupling in E and M.

The addition of a fifth, apical ligand to a planar ($\tau = 0°$) system of type I changes the symmetry from C_{2v} to C_s. In this latter symmetry, d_{xy} (a″ symmetry) cannot acquire components along the z axis because d_{xz} and d_{z^2} have the wrong symmetry (a′) to mix with d_{xy}. Although the addition of the fifth ligand raises the energy of d_{z^2}, this does not affect, to a first approximation, the in-plane unpaired electron density and hence the magnetic coupling. One compound that nicely exemplifies these concepts is $[Cu_2L'Cl_2]ClO_4$ (L′H = 2,6-bis[bis(2-pyridylmethyl)aminoethyl]-4-methylphenol). This dimer is formed by two undistorted tetragonal-pyramidal moieties that share the phenolic oxygen at the axial position and exhibits $-2J = 0$ cm^{-1}.[24]

In conclusion, the present results and considerations show that weak, axial bonds have a well-defined effect on magnetic coupling in doubly bridged, tetrahedrally distorted copper(II) dimers. The effect is clearly discernible in the E and M compounds, i.e. even when the dihedral τ angle is small, 14°.

Registry No. E, 116887-97-9; M, 116887-98-0; LH, 116865-23-7; 1,4-diazacycloheptene, 505-66-8; salicylaldehyde, 90-02-8.

Supplementary Material Available: Listings of thermal parameters and hydrogen atom coordinates, complete lists of bond lengths and angles, and a table of least-squares planes and deviations therefrom (7 pages); tables of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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