Synthesis, Magnetic, and Structural Characterization of Di-μ-(benzyloxo)-bis[(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II)]

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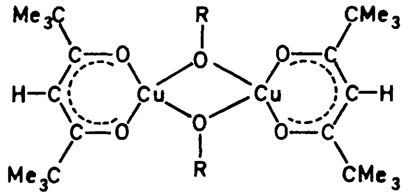
The synthesis of the title compound is reported. The crystal and molecular structure of the dimer has been determined from three-dimensional counter *X*-ray data. The compound crystallizes in the triclinic space group $P\bar{1}$ with one dimeric unit in a cell of dimensions a = 13.462(5), b = 6.064(2), c = 12.756(6) Å, α = 82.13(4), β = 115.61(2), and γ = 90.56(3)°. Least-squares refinement of the structure based on 1 575 observations has led to an *R* factor (on *F*) of 0.065. The compound consists of discrete dimeric units which are well separated from each other. The geometry around copper is approximately square planar, with Cu–O distances ranging from 1.883(5) to 1.910(5) Å; Cu–Cu 2.970(2) Å, Cu–O–Cu 102.1(2)°. The magnetic susceptibility of a powdered sample has been examined in the range 96.9—300.0 K. The dimer exhibits a large antiferromagnetic exchange interaction, the best fit to the Van Vleck dimer equation yielding $2J = -647$ cm^{-1} with $\langle g \rangle = 2.18$. This magnitude of $2J$ is much larger than that observed for analogous hydroxide-bridged compounds, and is taken as evidence in support of the conclusion that enhanced electron density at the bridge causes an increase in $|J|$.

THE structural and magnetic properties of many oxygen-bridged copper(II) dimers containing the Cu_2O_2 bridging system have been investigated previously in an effort to understand the factors influencing spin–spin interactions.[1-6] It is now generally accepted that the spin coupling found in these compounds occurs through the bridging groups by a σ pathway. In square-planar hydroxide-bridged compounds of the type $[\{CuL(OH)\}_2]^{2+}$ (L = a bidentate ligand) it has been found that the isotropic exchange parameter, $2J$, is linearly related to the Cu–O–Cu bridging angle, ϕ,[1,5] and this correlation has been explained in terms of molecular-orbital theory.[6] It should be noted, however, that while ϕ is very important, it is not the only structural parameter which can affect the value of $2J$. Sinn and his co-workers[4,7-12] have demonstrated that distortions from planar (towards tetrahedral) ligand environments at the metal centre also markedly affect the magnitude of J, although they may not change its sign.[13]

Another factor which would be expected to influence[1,14,15] the magnitude of $2J$, but which has not been well investigated to date, is the effect of changing the electron density at the bridging atoms. The concept that such changes affect $2J$ has received direct experimental support from recent studies on alkoxide-bridged chromium(III) dimers,[16,17] where it was shown that a change from methoxide to ethoxide bridges with no other structural change brings about an increase in the magnitude of $2J$; this, of course, parallels the greater base strength of ethoxide than methoxide ion.

This approach of altering the electron density at the bridging atoms by varying alkoxides within a homologous series of alkoxide-bridged compounds is appealing. Several years ago McWhinnie reported[18,19] the magnetic behaviour of a series of alkoxide-bridged compounds of the type $[\{Cu(ap)(OR)\}_2][NO_3]_2$ (ap = 2-aminopyridine). Unfortunately, no structural information is available for these compounds. Several structural and magnetic studies have been performed on alkoxide-bridged compounds of the type [CuX(OR)] (ROH = an amino-alcohol, X^- = a uninegative ligand such as Br^-).[2,20-27] In this series no linear relationship between ϕ and $2J$ has been found, presumably because in some of these compounds the Cu_2O_2 rings are strongly distorted from planarity while in others the neighbouring dimeric units are so close that they are able to form tetramers.[2,22,25,28-30] We therefore sought to study a different series of alkoxide-bridged copper(II) dimers.

We have investigated the preparation and characterization of a series of dimers of the type $[\{Cu(tmhd)(OR)\}_2]$ (1) (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate). Such a series should be useful in systematically testing the effects on $2J$ of variations in the electron density at the bridging oxygen atoms. As part of these studies we report the synthesis, magnetic properties, and structure of one of these compounds, di-μ-(benzyloxo)-bis[(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II)] (1; R = CH_2Ph).



(1)

EXPERIMENTAL

2,2,6,6-Tetramethylheptane-3,5-dione (Htmhd), was obtained from Aldrich Chemical Co, copper(II) acetate monohydrate from J. T. Baker Chemical Co., and benzyl alcohol from Fisher Scientific Co.

Di-μ-(benzyloxo)-bis[(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II)] (1; R = CH_2Ph).—The complex was prepared by recrystallization of [Cu(tmhd)(OMe)] from hot benzyl alcohol at temperatures < 140 °C. The process was repeated twice to give purple crystals (Found: C, 61.15; H, 7.45; Cu, 17.75. Calc. for $C_{36}H_{52}Cu_2O_6$: C, 61.1; H, 7.40; Cu, 17.95%).

[Cu(tmhd)(OMe)].—The complex was prepared by dropwise addition of a solution of sodium metal (0.54 g) in anhydrous methanol (20 cm^3) to bis(2,2,6,6-tetramethylheptane-3,5-dionato)copper(II) (10 g) in refluxing methanol (150 cm^3). After refluxing for 2 h, the mixture was filtered while hot, yielding a blue microcrystalline solid.

Copper analyses were obtained on a Sargent–Welch analyzer with platinum electrodes. Carbon and hydrogen analyses were performed by Galbraith Laboratories.

X-*Ray Data Collection.*—Purple needle-shaped crystals of (1; R = CH_2Ph) were obtained by slow evaporation of solvent from a solution of the compound in benzene and benzyl alcohol. The crystals showed a strong tendency toward twinning, and initial attempts to obtain crystals yielded some of marginal quality. On the basis of precession and Weissenberg photographs, the crystals were assigned to the triclinic system. No systematic absences were observed, which suggested that the space group was either $P1$ or $P\bar{1}$. The latter space group was chosen, and subsequent refinement indicated that it was the correct one. The cell constants were obtained by least-squares methods.

Crystal data. $C_{36}H_{52}Cu_2O_6$, a = 13.462(5) Å, b = 6.064(2), c = 12.756(6) Å, α = 82.13(4), β = 115.61(2), and γ = 90.56(3)°, at 21 °C, D_m = 1.24(3) (flotation in aqueous $ZnCl_2$), Z = 1, D_c = 1.268 g cm^{-3}, $\lambda(Cu\text{-}K_{\alpha 1})$ = 1.540 5 Å. In the centrosymmetric space group $P\bar{1}$ the dimer is constrained to lie on a crystallographic inversion centre.

Diffraction data were collected from a needle-shaped crystal with hexagonal cross sections which was mounted along the needle axis. The hexagonal faces were (010) and (0$\bar{1}$0); the six rectangular faces were (100), ($\bar{1}$00), (10$\bar{1}$), ($\bar{1}$01), (001), and (00$\bar{1}$). The distances between opposite pairs of faces were as follows: (100) to ($\bar{1}$00), 0.11; (10$\bar{1}$) to ($\bar{1}$01), 0.15; (001) to (00$\bar{1}$), 0.15; (010) to (0$\bar{1}$0), 0.65 mm.

Intensity data were collected on a Picker four-circle automatic diffractometer using Cu-K_α radiation. The mosaicicity of the crystal was examined by means of the narrow source open-counter ω-scan technique and was judged to be acceptable. Twelve reflections, accurately centred through a narrow vertical slit at a take-off angle of 1.0°, formed the basis of the least-squares refinement of cell parameters and orientation using the logic documented by Busing and Levy for the PDP-8/L computer.[31] Intensity data were collected at a take-off angle of 3.0°; at this angle the intensity of a typical reflection was *ca.* 90% of the maximum as a function of take-off angle. The counter aperture was 5.0 × 5.0 mm and was positioned 32 cm from the crystal. The radiation was filtered by nickel foil (0.5 × 10^{-3} in). The data were collected by the θ—2θ scan technique at a scan rate of 1° min^{-1}. The peaks were scanned from 1.0° in 2θ below the calculated $K_{\alpha 1}$ peak position to 1.0° in 2θ above the calculated $K_{\alpha 2}$ position. Stationary-counter–stationary-crystal background counts of 20 s were taken at each end of the scan. The pulse-height analyzer was set for a *ca.* 90% window, centred on the Cu-K_α peak.

A unique data set having $3° \leqslant 2\theta \leqslant 107°$ and consisting of 2 080 recorded intensities was collected. The intensities of three standard reflections, measured after every 100 reflections, showed no appreciable decrease throughout the run.

Solution and refinement of the structure. Data processing was carried out as described by Corfield *et al.*[32] After correction for background, the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(t_s/t_b)^2(BH + BL) + (pI)^2]^{\frac{1}{2}}$ where the symbols have the meanings defined in ref. 32 and the value of p was selected as 0.060. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption factors. The absorption coefficient for this compound for Cu-K_α radiation is 16.36 cm^{-1}; the transmission coefficients ranged from 0.69 to 0.88. Of the 2 080 data collected, 1 575 had intensities which were greater than three times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.

The position of the copper atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement were carried out on this position. At this stage the agreement factors $R(= \Sigma||F_o| - |F_o||/\Sigma|F_o|)$ and $R'\{= \Sigma w[(|F_o| - |F_c|)^2/w(F_o)^2]^{\frac{1}{2}}\}$ were 0.460 and 0.509, respectively. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights, w, being as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for the non-hydrogen atoms were from International Tables,[33a] while the scattering factors for hydrogen were from Stewart *et al.*[33b] The effects of the anomalous dispersion of copper were included in the calculations of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from ref. 34.

Subsequent difference-Fourier maps revealed the positions of the remaining non-hydrogen atoms. Isotropic least-squares refinement of the non-hydrogen atoms gave R = 0.123 and R' = 0.171. Anisotropic refinement of the non-hydrogen atoms gave R = 0.085 and R' = 0.118. The positions of H(1A) and H(1B) were revealed in the difference-Fourier maps as were peaks between the t-butyl methyl-carbon atoms, which were attributed to disorder. These methyl-carbon atom peaks were *ca.* 25% of the height of the methyl-carbon atom peaks that had been located earlier. The two sets of t-butyl methyl-carbon atoms were consequently assigned relative weights of 0.2 and 0.8. These weights were not varied in subsequent refinement. In the light of the disorder of the t-butyl groups, no effort was made to locate the 36 t-butyl hydrogen atoms in the molecule. Hydrogen atom H(5) was placed in a calculated position assuming trigonal geometry at carbon atom C(5)

TABLE 1

Positional parameters for [{Cu(tmhd)(OCH_2Ph)}$_2$]

Atom	*x/a*	*y/b*	*z/c*
Cu	0.102 4(1)	0.095 7(2)	0.079 7(1)
O(2)	−0.053 8(4)	0.120 1(9)	0.025 5(4)
C(1)	−0.115 4(6)	0.291 4(12)	0.036 4(6)
O(3)	0.131 3(4)	0.283 8(8)	0.195 1(4)
C(4)	0.226 5(6)	0.332 0(12)	0.267 3(5)
C(5)	0.323 0(5)	0.272 3(13)	0.264 7(6)
C(6)	0.331 3(6)	0.148 2(13)	0.185 1(7)
O(7)	0.250 6(4)	0.068 6(9)	0.105 3(4)
C(8)	0.223 3(6)	0.461 0(13)	0.360 1(6)
C(9A)	0.180 7(14)	0.305 9(23)	0.437 2(11)
C(10A)	0.137 6(12)	0.654 2(21)	0.300 0(10)
C(11A)	0.338 8(9)	0.535 5(26)	0.439 6(12)
C(9B)	0.297 3	0.341 7	0.479 1
C(10B)	0.105 1	0.479 0	0.349 3
C(11B)	0.283 8	0.671 4	0.366 8
C(12)	0.444 4(7)	0.098 3(15)	0.184 4(8)
C(13A)	0.455 7(10)	−0.148 7(20)	0.177 6(14)
C(14A)	0.444 5(10)	0.240 7(23)	0.076 6(12)
C(15A)	0.543 8(8)	0.162 3(28)	0.259 9(12)
C(13B)	0.513 2	−0.048 7	0.296 8
C(14B)	0.427 7	−0.024 1	0.080 0
C(15B)	0.505 2	0.301 8	0.181 1
H(1A)	−0.195 1	0.335 9	−0.031 6
H(1B)	−0.085 4	0.471 2	0.029 8
H(5)	0.392 1	0.317 0	0.321 5

and a C–H bond length of 0.95 Å. In subsequent refinements, the isotropic thermal parameters but not the positions of H(1A), H(1B), H(5) and the methyl-carbon atoms (weight 0.2) were varied, while the phenyl ring was refined isotropically as a planar group (C–C 1.390, C–H 0.95 Å) and the remaining atoms were refined anisotropically. The final values of R and R' were 0.065 and 0.085 based on 1 575 intensities and 170 variables. In the final cycle of least-squares refinement no parameter experienced a shift of more than 0.03 σ, which indicates convergence. The positional parameters, together with their standard deviations as estimated from the inverse matrix, are listed in Table 1 and the derived positional parameters for the atoms in the phenyl group are in Table 2. The atomic thermal parameters and a compilation of observed and calculated structure amplitudes are available as Supplementary Publication No. SUP 22444 (14 pp.).*

TABLE 2

Derived parameters for phenyl-ring atoms *

Atom	x/a	y/b	z/c
C(1P)	−0.1306	0.2572	0.1469
C(2P)	−0.1752	0.4335	0.1749
C(3P)	−0.1899	0.4070	0.2771
C(4P)	−0.1601	0.2042	0.3514
C(5P)	−0.1155	0.0279	0.3234
C(6P)	−0.1008	0.0544	0.2212
H(2P)	−0.1955	0.5720	0.1242
H(3P)	−0.2204	0.5274	0.2963
H(4P)	−0.1702	0.1861	0.4213
H(5P)	−0.0951	0.1106	0.3742
H(6P)	−0.0703	−0.0660	0.2020

* The refined group parameters (as defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 773) are $x_c = -0.145\,3(3)$, $y_c = 0.230\,7(6)$, $z_c = 0.249\,2(3)$, $\delta = -2.757(3)$, $\varepsilon = -3.080(3)$, and $\eta = 1.457(3)$.

DISCUSSION

Description of the Structure of [{Cu(tmhd)(OCH$_2$Ph)}$_2$].—The compound consists of discrete dimeric units which are well separated from one another. The geometry of the dimer is shown in Figure 1. The interatomic bond distances and angles are given in Tables 3 and 4, respectively. The general structure of [{Cu(tmhd)(OCH$_2$Ph)}$_2$] differs from that of the corresponding pentane-2,4-dionato-compound, [Cu(pd)(OCH$_2$Ph)], which is a tetramer.[3] In the latter case, a methyl group of one pd ligand sits immediately above another pd ligand in the tetramer. The larger spatial demands of the t-butyl groups in the tmhd compound compared to the methyl groups in its pd analogue apparently preclude such tetramer formation in the former.

TABLE 3

Interatomic bond distances (Å)

Cu–Cu′	2.970(2)	C(8)–C(9A)	1.551(13)
Cu–O(2)	1.908(5)	C(8)–C(9B)	1.492(7)
Cu–O(2′)	1.910(5)	C(8)–C(10A)	1.519(13)
Cu–O(3)	1.891(5)	C(8)–C(10B)	1.541(7)
Cu–O(7)	1.883(5)	C(8)–C(11A)	1.549(12)
O(2)–C(1)	1.394(8)	C(8)–C(11B)	1.499(7)
C(1)–C(1P)	1.497(8)	C(12)–C(13A)	1.526(14)
O(3)–C(4)	1.273(8)	C(12)–C(13B)	1.492(9)
C(4)–C(5)	1.367(9)	C(12)–C(14A)	1.520(14)
C(4)–C(8)	1.521(9)	C(12)–C(14B)	1.543(8)
C(5)–C(6)	1.386(10)	C(12)–C(15A)	1.569(13)
C(6)–O(7)	1.271(8)	C(12)–C(15B)	1.480(9)
C(6)–C(12)	1.559(10)		

TABLE 4

Intramolecular bond angles (°)

O(2)–Cu–O(2′)	77.9(2)	C(5)–C(6)–C(12)	121.5(7)
O(2)–Cu–O(3)	94.2(2)	O(7)–C(6)–C(12)	113.4(7)
O(2′)–Cu–O(7)	94.5(2)	C(6)–O(7)–Cu	125.2(5)
O(3)–Cu–O(7)	94.1(2)	C(4)–C(8)–C(9A)	108.0(7)
Cu–O(2)–Cu′	102.1(2)	C(4)–C(8)–C(10A)	109.0(6)
Cu–O(2)–C(1)	127.2(4)	C(4)–C(8)–C(11A)	112.0(7)
Cu′–O(2)–C(1)	128.7(4)	C(4)–C(8)–C(9B)	109.2(6)
O(2)–C(1)–C(1P)	114.5(6)	C(4)–C(8)–C(10B)	110.4(5)
C(1)–C(1P)–C(2P)	118.7(6)	C(4)–C(8)–C(11B)	112.1(5)
C(1)–C(1P)–C(6P)	121.3(6)	C(6)–C(12)–C(13A)	108.9(7)
Cu–O(3)–C(4)	125.7(5)	C(6)–C(12)–C(14A)	107.2(7)
O(3)–C(4)–C(5)	124.4(6)	C(6)–C(12)–C(15A)	112.0(7)
O(3)–C(4)–C(8)	113.2(6)	C(6)–C(12)–C(13B)	107.1(6)
C(5)–C(4)–C(8)	122.4(6)	C(6)–C(12)–C(14B)	110.3(6)
C(4)–C(5)–C(6)	125.0(6)	C(6)–C(12)–C(15B)	112.7(6)
C(5)–C(6)–O(7)	125.1(7)		

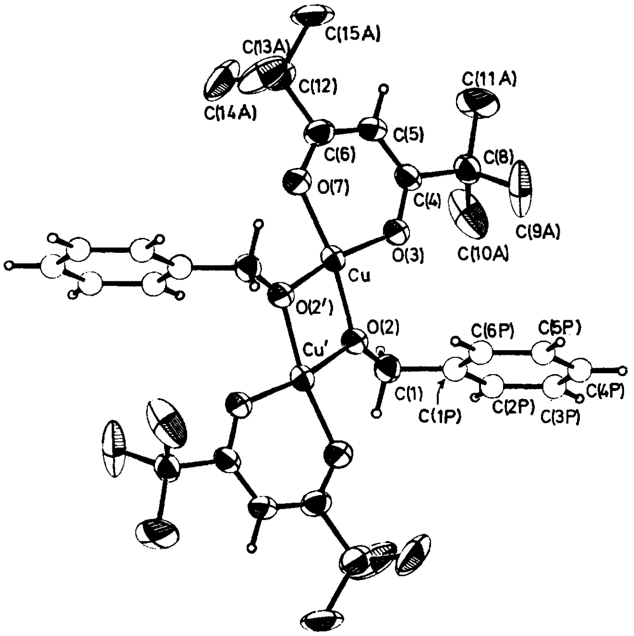


FIGURE 1 View of the dimeric [{Cu(tmhd)(OCH$_2$Ph)}$_2$] molecule. Only the anisotropically refined t-butyl carbon atoms are shown. Unlabelled atoms are related to labelled atoms by the inversion centre. The thermal ellipsoids of the non-hydrogen atoms are drawn at the 40% probability level; the hydrogen atoms are of arbitrary size

The Cu$_2$O$_2$ bridging group in [{Cu(tmhd)(OCH$_2$Ph)}$_2$] is exactly planar because of the crystallographic centre of inversion. The Cu–Cu separation [2.970(2) Å] is in the ranges found for hydroxide-bridged copper(II) dimers (2.847—3.00 Å) and for alkoxide-bridged copper(II) dimers of the type [{CuX(OR)}$_2$] (X = Cl, Br, NO$_2$, or SCN; ROH = an amino-alcohol), 2.903—3.026 Å (see Table 5). The Cu–O–Cu bridging angle, ϕ, is 102.1(2)°, which is also in the range found for other hydroxide and alkoxide-bridged copper(II) dimers (Table 5). In the corresponding pd tetramer, [{Cu(pd)(OCH$_2$Ph)}$_4$], the Cu–O–Cu angle is 105.8° for the bridging oxygen atom that is bonded to two copper atoms and 100.9° for the other which is bonded to three.[3]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 5

Bridging geometry and singlet- triplet splitting ($2J$) for hydroxide- and alkoxide-bridged copper(II) dimers

Compound	Cu–Cu(Å)	$\phi/°$	$2J/\text{cm}^{-1}$	Ref.
$[\{Cu(bipy)(OH)\}_2][NO_3]_2$	2.847	95.6	+172	*a*
$[\{Cu(bipy)(OH)\}_2][SO_4]\cdot 5H_2O$	2.893	97.0	+49	*b*
$[\{Cu(eaep)(OH)\}_2][ClO_4]_2$	2.917	99.2	−130	14, *c*
β-$[\{Cu(dmaep)(OH)\}_2][ClO_4]_2$	2.935	100.4	−201	35
$[\{Cu(tmen)(OH)\}_2][NO_3]_2$	2.954	101.9	−367	2
$[\{Cu(tmen)(OH)\}_2][ClO_4]_2$	2.966	102.3	−360	6, *d*
α-$[\{Cu(teen)(OH)\}_2][ClO_4]_2$	2.978	103.0	−410	5, *e*
β-$[\{Cu(teen)(OH)\}_2][ClO_4]_2$	2.997	103.7	−469	2
$[\{Cu(tmen)(OH)\}_2]Br_2$	3.000	104.1	−509	*f*
$[\{Cu(deae)Cl\}_2]$	2.935	96.6	−99	22, 23
$[\{Cu(deap)Cl\}_2]$	2.903	97.9	−149	2
$[\{Cu(deae)(SCN)\}_2]$	2.981	101.5	−250	21, 23
$[\{Cu(deap)Br\}_2]$	2.911	100.0	−338	2
$[\{Cu(deae)(NO_2)\}_2]$	2.976	102.3	−361	2
$[\{Cu(deae)Br\}_2]$	3.026	104.5	−799	20, 24

bipy = 2,2′-Bipyridine, eaep = 2-(2-ethylaminoethyl)pyridine, dmaep = 2-(2-dimethylaminoethyl)pyridine, tmen = *NNN′N*-tetramethylethylenediamine, teen = *NNN′N′*-tetraethylethylenediamine, deae = 1-diethylaminoethanolate, deap = 1-diethylaminopropan-2-olate.

[a] K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem. Letters*, 1973, **9**, 423; R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74**, 2497. [b] J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 144; A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 904; B. F. Hoskins and F. D. Whillans, *J.C.S. Dalton*, 1975, 1267; A. T. Casey, *Austral. J. Chem.*, 1972, **25**, 2311; J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Comm.*, 1970, 1593. [c] D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 2216. [d] S. F. Pavkovic, personal communication. [e] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, 1963, **2**, 629. [f] J. R. Wasson, T. P. Mitchell, and W. H. Bernard, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2865; T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Cryst.*, 1970, **B26**, 2096; B. J. Cole and W. H. Brumage, *J. Chem. Phys.*, 1970, **53**, 4718.

The four oxygen atoms co-ordinated to each copper and the copper atom lie approximately in a plane (plane 3, Table 6). The deviation from planarity can be described in terms of the angle between the O(2)–Cu–O(2′) and O(3)–Cu–O(7) planes, τ, which is 10.2°. Sinn and his co-workers[3,7-12] have noted that such distortions from planarity toward a tetrahedral environment around the copper atom have the effect of reducing the strength of antiferromagnetic interactions between copper atoms. However, this distortion is slight in the present compound; moreover, it is similar to the distortions found in hydroxide-bridged dimers. For example, we have calculated τ values of 6.3 and 7.7° for β-$[\{Cu(dmaep)(OH)\}_2][ClO_4]_2$ and $[\{Cu(teen)(OH)\}_2][ClO_4]_2$, respectively.* We can therefore expect the changes in spin coupling through the $[\{Cu(tmhd)(OR)\}_2]$ series to reflect primarily changes in ϕ and in electron density at the bridges due to changes in R. In the benzyloxo-compound, we note that the magnetic-susceptibility data (see below) yield a $2J$ value of −647 cm^{-1}; the magnitude of J is far in excess of that observed for hydroxide-bridged dimers with comparable ϕ values (see Table 5) or the value of −339.5 cm^{-1} predicted from the linear relationship between J and ϕ observed for those compounds.[6] Hence, it is evident, that in this case the enhanced electron density at the bridge brought about by the greater electron-donating ability of $[OCH_2Ph]^-$ than that of $[OH]^-$ has a marked influence on the magnitude of the magnetic exchange.

TABLE 6

Least-squares planes in $[\{Cu(tmhd)(OCH_2Ph)\}_2]$

Plane 1		Plane 2		Plane 3	
atom	deviation (Å)	atom	deviation (Å)	atom	deviation (Å)
O(3) *	0.012	Cu *	0.000	Cu *	0.009
C(4) *	−0.013	O(2) *	0.000	O(2) *	0.119
C(5) *	−0.001	Cu′ *	0.000	O(2′) *	−0.107
C(6) *	0.014	O(2′) *	0.000	O(3) *	0.102
O(7) *	−0.012	C(1)	0.288	O(7) *	−0.123
Cu	0.117	O(3)	−0.265	C(1)	0.543
O(2)	−0.056	O(7)	0.221	C(4)	−0.244
C(8)	0.083			C(6)	−0.012
C(12)	0.103				

* Atom included in the calculation of the plane.

The plane defined by Cl and the phenyl ring makes an angle of 93.8° with the Cu_2O_2 unit. The O(2)–Cl distance [1.394(8) Å] is appreciably shorter than the corresponding distance reported for $[\{Cu(pd)(OCH_2Ph)\}_4]$ [1.49(2) Å][3] but seems very reasonable to us. By comparison, the bridging-oxygen-to-carbon distance reported for $[\{Cu(deap)Cl_2\}]$ (deap = 1-diethylaminopropan-2-olate) is 1.421(18) Å.[2]

The O–C–C–C–O portion of the diketone ring is planar, no atom deviating by >0.014 Å from the least-squares plane through these atoms (plane 1, Table 6). The copper atom sits 0.117 Å above this plane. The central carbon atoms of the t-butyl groups, C(8) and C(12), are situated 0.083 and 0.103 Å, respectively, above the plane. Within the level of significance suggested by the estimated standard deviations, the copper–diketonate ring is symmetric. The bond angles and distances within the ring agree with those reported for other copper–diketonate and other metal–tmhd structures.[3,36-38] For example, the average (1.887 Å) of the Cu–O(3) and Cu–O(7) distances agrees well with the corresponding copper–oxygen distances in $[Cu(3Ph\text{-}pd)_2]$ (1.90 Å)[37] and in $[\{Cu(pdc)(OCH_2Ph)\}_4]$ (1.90 Å).[3]

Because of disorder and large thermal motion, the methyl-carbon atom positions of the t-butyl groups are poorly determined. The average $C\text{–}CH_3$ distance for the anisotropically refined methyl carbon atoms is 1.539 ± 0.017 Å (error limits are the average deviation

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* Values calculated from the data in refs. 35 and 5, respectively. dmaep = 2-(2-Dimethylaminoethyl)pyridine and teen = *NNN′N′*-tetraethylethylenediamine.

from the mean), while the corresponding distance for the isotropically refined, weighted (0.2), methyl-carbon atoms is 1.508 ± 0.023 Å. The average CH_3-C-CH_3 angles are 109.4 ± 1.8 and 108.5 ± 4.0° for the anisotropically refined and the isotropically refined carbon atoms, respectively. The CH_3(A)-C-CH_3(B) angles average 56.1 ± 5.5°, which suggests that the two sets of disordered positions are composed of two approximately tetrahedral t-butyl groups which are in staggered orientations.

Magnetic Properties.—The magnetic susceptibility of a powdered sample of the dimeric compound was measured from 96.9 to 300.0 K on a Faraday balance [39] using mercury(II) tetrathiocyanatocobaltate(II) as the susceptibility standard.[40] The susceptibility data were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[41] The corrected data were fitted to the Bleaney–Bowers equation [42] (1) for two interacting $S = \frac{1}{2}$ centres where J is defined by the Hamiltonian (2).

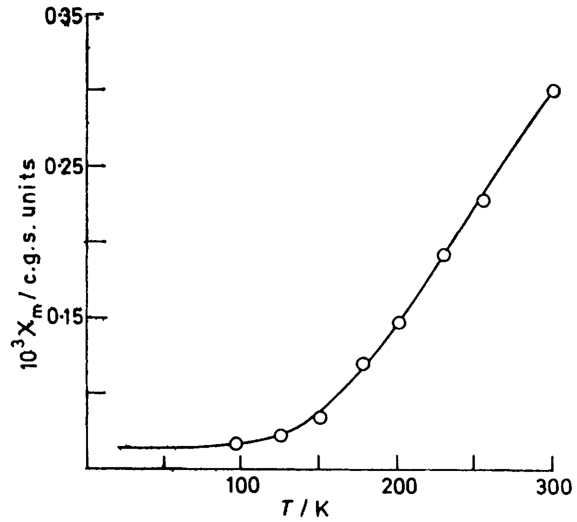

FIGURE 2 Temperature dependence of the magnetic susceptibility of [{Cu(tmhd)(OC_2Ph)}$_2$]. The experimental data are shown as circles, and the best fit to the dimer ($S = \frac{1}{2}, \frac{1}{2}$) equation is displayed as the full line

$$\chi_m = (g^2\beta^2N/3k\mathrm{T})[1 + (1/3)\exp(-2J/kT)]^{-1} + N\alpha \qquad (1)$$

$$H_{ex} = -2J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 \qquad (2)$$

The fit was accomplished by means of a non-linear least-squares procedure utilizing $\sum_i[\chi_m(\mathrm{expt.})_i - \chi_m(\mathrm{calc.})]_i^2T_i^2$ as the fitting criterion.[43] The data, which are presented in Figure 2, do not show a maximum in the temperature range available, but fit the above expression very well with $2J = -647$ cm^{-1}, $g = 2.18$, and $N\alpha = 64.7 \times 10^{-6}$ c.g.s. units. Hence, as was noted above, there is little doubt that the enhanced electron density at the bridge, as compared to a hydroxide-bridged species, brings about an increase in the magnitude of J.

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