Crystal and Molecular Structure and Magnetic Properties of Tris{di-μ-methoxo-bis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]dicopper(II)}†

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The crystal and molecular structure of $[\{Cu_2(OMe)_2(tftbd)_2\}_3]$ [tftbd = 4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate] has been determined from single-crystal *X*-ray diffraction data and refined to *R* 0.058 for 3 241 independent reflections. The compound crystallizes in the triclinic space group $P\bar{1}$ with one hexameric molecule in a cell of dimensions *a* = 11.212(7), *b* = 11.079(7), *c* = 15.315(9) Å, α = 92.71(5), β = 116.80(5), and γ = 95.56(5)°. The molecule consists of three roughly planar methoxo-bridged dimeric units: a centrosymmetric 'dimer' with average Cu–O 1.94(1) Å and Cu–O–Cu 99.5(3)° within the Cu_2O_2 bridging group, and two inversion-related non-centrosymmetric 'dimers' having a slightly non-planar Cu_2O_2 group with Cu–O ranging from 1.90(1) to 1.96(1) Å and two different Cu–O–Cu angles, 98.9(3) and 102.8(3)°. The dimers are joined by axial copper–oxygen bonds. The geometry around the copper atoms is approximately square pyramidal. Magnetic susceptibility data in the range 4.2—350 K indicate overall antiferromagnetic spin coupling. The magnetism of the complex can be explained using the isotropic Heisenberg–Dirac–van Vleck model for three non-interacting dimers. The resulting values for the exchange parameters indicate a stronger antiferromagnetic interaction in the non-symmetric 'dimer' ($J = -440$ cm^{-1}) than in the centrosymmetric one ($J = -214$ cm^{-1}). The magnetism of both 'dimers' is discussed in relation to the structural data.

The alkoxo-bridged copper(II) complexes are a large group of polynuclear compounds within which correlations between magnetic and structural data are being investigated.[1–7] This group includes numerous bi-, tetra-, and poly-nuclear complexes with polydentate ligands such as aminoalcohols[1,3] and Schiff bases[2] and only a few complexes of formula $[\{Cu_2(OR)_2L_2\}_n]$ containing the bridging group OR (R = Me, Et, Pr, or CH_2Ph) and a non-bridging ligand (L).[4–8] A common feature of these compounds is the presence of a Cu_2O_2 ring and antiferromagnetic interactions in binuclear complexes, as well as both antiferro- and ferro-magnetic interactions in tetranuclear complexes. A linear dependence of the singlet–triplet distance (*J*) on the Cu–O–Cu bridge angle was found for several alkoxo-bridged copper(II) dimers and tetramers built from weakly associated dimers.[1] Comparison between this dependence and that observed by Hatfield and co-workers[9] for hydroxo-bridged copper(II) dimers reveals the stronger interaction between copper(II) ions in the alkoxo-bridged cases. This confirms a suggestion[10] that the electron density on the bridging atom, which is modified by the group(s) attached to it, is another factor influencing the value of *J*, in addition to structural factors. In order to determine the relative importance of this factor, it is useful to investigate a series of alkoxo-bridged complexes with OR ions.

The present paper deals with the molecular structure and magnetic studies of a compound belonging to the series $[\{Cu_2(OR)_2L_2\}_n]$, where in this case L = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate (tftbd), R = Me, and *n* = 3. The structure of another member of this series with the same L, R = Et, and *n* = 4 has been reported.[5] The spectroscopic and magnetic properties of the present compound and other compounds with various β-diketonate anions as L, and R = Me or Et have been described.[11]

Results and Discussion

Description of the Structure.—The molecular structure is illustrated in Figures 1 and 2 and the atom co-ordinates and selected bond lengths and angles are given in Tables 1 and 2. The unit cell contains one centrosymmetric, hexanuclear molecule, which consists of three roughly planar methoxo-bridged dimers situated roughly parallel to one another but staggered. The dimers are joined by out-of-plane Cu–O bonds of length *ca.* 2.5 Å between the copper and methoxo-oxygen atoms and *ca.* 2.8 Å between the copper and β-diketonate oxygen atoms. Two crystallographically different 'dimers' exist in the hexanuclear molecule: a centrosymmetric, inner 'dimer' with a Cu(2)–O(3)–Cu(2′)–O(3′) ring in which the methoxo-oxygen atoms are four-co-ordinated, and an outer 'dimer' with a Cu(1)–O(2)–Cu(3)–O(1) ring in which one methoxo-oxygen atom, O(1), is four-co-ordinated and the second, O(2), is three-co-ordinated. The Cu · · · Cu distances in different dimeric units are the same [mean 2.964(2) Å]. On the other hand, the geometries of the Cu_2O_2 rings in the two 'dimers' are slightly different. The centrosymmetric Cu_2O_2 ring in the inner 'dimer' has an average Cu–O bond length of 1.95(1) Å and a Cu–O–Cu bridge angle of 99.5(3)°. In the outer 'dimer' the two longer Cu–O bonds [mean 1.95(1) Å] involving O(1) and two shorter ones [mean 1.90(1) Å] involving O(2) form a non-symmetric, slightly non-planar Cu_2O_2 ring with two different Cu–O–Cu angles, 98.9(3) and 102.8(3)° for O(1) and O(2), respectively.

The arrangement of bonds around the four-co-ordinated methoxo-oxygen atoms, O(1) and O(3), is roughly tetrahedral. The methoxo-carbon atom C(1) is 0.83 Å out of the Cu(1)–O(1)–Cu(3) plane and C(3) is 0.75 Å out of the Cu(2)–O(3)–Cu(2′) plane. The three bonds around the O(2) methoxo-oxygen atom are essentially planar.

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† *Supplementary data available* (No. SUP 56340, 28 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. ≈ 9.27×10^{-24} A m^2.

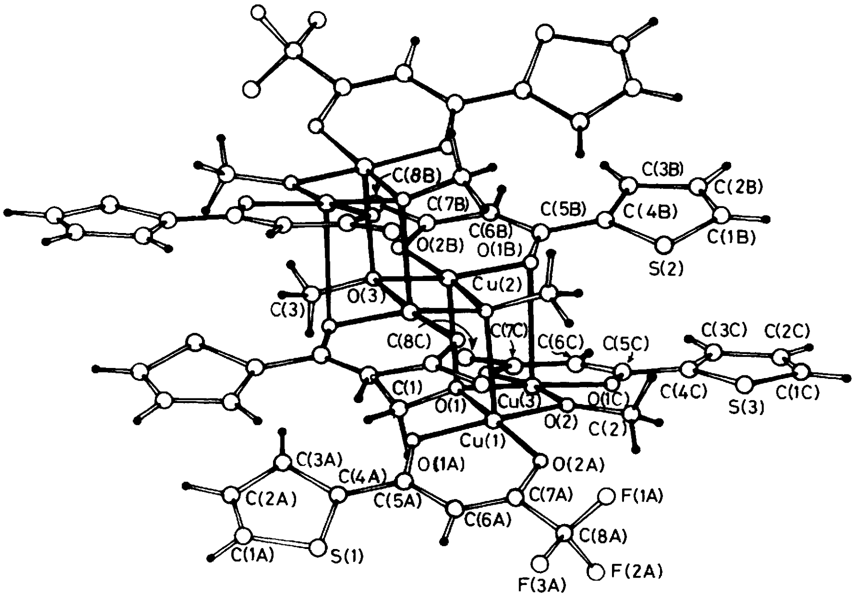


Figure 1. Molecular structure of [{$Cu_2(OMe)_2(tftbd)_2$}$_3$]. Unlabelled atoms are related to labelled atoms by the inversion centre. Fluorine atoms attached to C(8B) and C(8C) are omitted for clarity

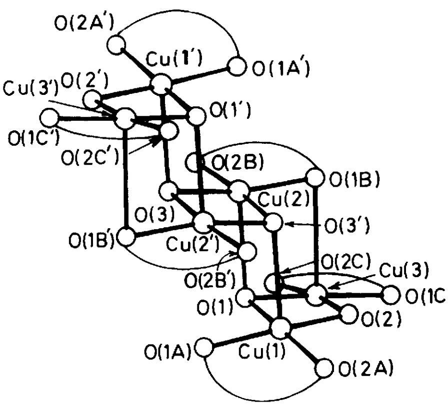


Figure 2. Co-ordination around the copper centres in [{$Cu_2(OMe)_2(tftbd)_2$}$_3$]

The three independent copper centres have essentially a square-pyramidal co-ordination with different degrees of distortion. The four nearest oxygen atoms around Cu(1) lie on a plane within experimental error, Cu(1) being displaced 0.128(2) Å from this plane towards the top of a pyramid. The atom Cu(3) lies approximately in the basal plane, the maximum deviation of the five atoms from this mean plane being *ca.* 0.08 Å. The co-ordination geometry around the copper atom of the inner 'dimer', Cu(2), is less simple. The basal plane shows a small tetrahedral distortion with the dihedral angle between the CuO_2 planes equal to 12°. The fifth co-ordination site is occupied by the methoxo-oxygen O(1) from the adjacent dimer. The β-diketonate oxygen atom, O(1A'), is situated on the side opposite to the pyramid apex at a distance of 3.02(1) Å, indicative of only a weak interaction.

The dimensions of the three independent tftbd systems are in mutual agreement and are comparable with previous results.[5,12] During the refinement some degree of disorder of the thienyl group of the β-diketonate ligand denoted as A was apparent. As a consequence the bond lengths and angles within this group are of limited accuracy. The thienyl ring and the O–C–C–C–O skeleton of the chelate ring of each β-diketonate ligand are planar within experimental error and approximately coplanar. Although the ligand molecules are planar, neither of the dimeric units as a whole is strictly planar. The two chelate rings in the inner 'dimer' are twisted by 17° from the Cu_2O_2 ring plane. The non-planarity of the outer 'dimer' may be evaluated from the dihedral angles between some planes: *ca.* 10° between the two CuO_2 planes in the copper–oxygen ring, *ca.* 17° between the two basal copper co-ordination planes, and *ca.* 20° between the basal co-ordination plane of Cu(1) and that of its diketonate ligand.

Magnetic Properties.—The present compound exhibits rather strong antiferromagnetic interactions with a maximum magnetic susceptibility at *ca.* 280 K. The magnetic moment per copper(II) ion decreases with decreasing temperature from 1.3 B.M. at 340 K to a constant value of 1.1 B.M. at temperatures below 30 K. A small increase in magnetic susceptibility at the lowest temperatures is indicative of the presence of small amounts of paramagnetic impurities. Prior to theoretical analyses, the measured susceptibilities were corrected by 0.5% for the impurities, assuming that the susceptibilities at < 30 K result exclusively from monomeric copper(II) impurities.

The simplest isotropic Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian suitable for interpretation of the magnetic properties of the hexanuclear cluster is as in equation (1) where

$$\mathcal{H} = -J_aS_3S_4 - J_b(S_1S_2 + S_5S_6) - J_c(S_2S_3 + S_4S_5) - J_d(S_1S_3 + S_4S_6) - J_e(S_2S_4 + S_3S_5) \quad (1)$$

S_i is the spin on centre i, the coefficient J to S_iS_j is an exchange coupling parameter, and the subscripts refer to the individual copper ions numbered as shown below. It is not possible to obtain explicit formulae for the eigenvalues of this Hamiltonian in terms of spin values and exchange parameters. The more general procedure of Sinn[13] is necessary in this case. However, application of multi-parameter models often leads to overparametrization. It seems that, in view of the experimental errors, it is safer to use simpler models, where justified. The present hexanuclear cluster is formed by association of dimeric units in which the basically square-pyramidal environment of

Table 1. Atomic positional parameters with estimated standard deviations in parentheses for $[\{Cu_2(OMe)_2(tftbd)_2\}_3]$

Atom	*x*	*y*	*z*
Cu(1)	0.722 82(13)	0.133 25(11)	0.460 59(9)
Cu(2)	0.406 07(13)	0.021 10(11)	0.398 25(9)
Cu(3)	0.530 67(13)	0.175 80(11)	0.258 07(9)
O(1)	0.5820(6)	0.0418(5)	0.3388(4)
O(2)	0.6496(6)	0.2610(5)	0.3826(5)
O(3)	0.4542(6)	−0.1112(5)	0.4824(4)
O(1A)	0.7947(6)	−0.0121(5)	0.5206(5)
O(2A)	0.8706(7)	0.2420(6)	0.5629(5)
O(1B)	0.3420(6)	0.1665(5)	0.3349(5)
O(2B)	0.2750(6)	−0.0866(5)	0.2870(5)
O(1C)	0.4944(7)	0.3218(5)	0.1932(4)
O(2C)	0.4288(7)	0.0709(5)	0.1381(4)
S(1)	1.1082(4)	−0.1611(4)	0.6918(4)
S(2)	0.3013(3)	0.4185(3)	0.3057(3)
S(3)	0.4817(4)	0.5760(3)	0.1582(3)
C(1)	0.5950(10)	−0.0721(8)	0.2978(7)
C(2)	0.6869(11)	0.3890(9)	0.4075(8)
C(3)	0.4609(11)	−0.2313(8)	0.4483(7)
C(1A)	1.0704(12)	−0.3096(9)	0.6733(9)
C(2A)	0.9462(13)	−0.3461(10)	0.6054(9)
C(3A)	0.8530(7)	−0.2564(5)	0.5518(5)
C(4A)	0.9519(9)	−0.1389(9)	0.6064(7)
C(5A)	0.9155(10)	−0.0153(8)	0.5845(7)
C(6A)	1.0076(9)	0.0908(8)	0.6365(6)
C(7A)	0.9798(9)	0.2046(8)	0.6237(7)
C(8A)	1.0889(10)	0.3105(9)	0.6824(8)
C(1B)	0.2023(12)	0.5125(9)	0.2340(9)
C(2B)	0.0939(12)	0.4552(10)	0.1525(8)
C(3B)	0.0825(10)	0.3233(8)	0.1453(7)
C(4B)	0.1990(9)	0.2910(8)	0.2295(6)
C(5B)	0.2347(9)	0.1710(8)	0.2553(6)
C(6B)	0.1545(9)	0.0673(9)	0.1924(6)
C(7B)	0.1830(9)	−0.0495(8)	0.2122(6)
C(8B)	0.0939(10)	−0.1560(9)	0.1356(7)
C(1C)	0.4113(13)	0.6731(9)	0.0762(9)
C(2C)	0.3214(13)	0.6196(10)	−0.0141(9)
C(3C)	0.3050(10)	0.4879(8)	−0.0201(7)
C(4C)	0.3938(9)	0.4525(8)	0.0728(7)
C(5C)	0.4161(10)	0.3304(8)	0.1040(7)
C(6C)	0.3489(10)	0.2279(8)	0.0322(7)
C(7C)	0.3633(10)	0.1099(8)	0.0550(7)
C(8C)	0.2918(11)	0.0081(9)	−0.0301(7)
F(1A)	1.0469(7)	0.3912(6)	0.7250(5)
F(2A)	1.1320(9)	0.3704(8)	0.6307(6)
F(3A)	1.1928(7)	0.2767(6)	0.7573(6)
F(1B)	0.1640(7)	−0.2271(5)	0.1120(5)
F(2B)	0.0014(6)	−0.1223(5)	0.0523(4)
F(3B)	0.0254(7)	−0.2267(5)	0.1705(5)
F(1C)	0.2343(10)	0.0458(6)	−0.1156(5)
F(2C)	0.3734(7)	−0.0688(6)	−0.0300(6)
F(3C)	0.1955(7)	−0.0589(7)	−0.0215(6)

Table 2. Selected bond distances (Å) and angles (°) with standard deviations in parentheses

(*a*) In the co-ordination polyhdedrons

Cu(1)–O(1)	1.963(6)	Cu(2)–O(3)	1.951(5)	Cu(3)–O(1)	1.939(5)
Cu(1)–O(2)	1.898(6)	Cu(2)–O(3′)	1.932(5)	Cu(3)–O(2)	1.896(6)
Cu(1)–O(1A)	1.952(6)	Cu(2)–O(1B)	1.948(6)	Cu(3)–O(1C)	1.919(6)
Cu(1)–O(2A)	1.935(6)	Cu(2)–O(2B)	1.923(6)	Cu(3)–O(2C)	1.918(6)
Cu(1)–O(3′)	2.499(7)	Cu(2)–O(1)	2.515(7)	Cu(3)–O(1B)	2.843(7)
O(1)–Cu(1)–O(2)	78.3(3)	O(3)–Cu(2)–O(3′)	80.5(3)	O(1)–Cu(3)–O(2)	78.0(3)
O(2)–Cu(1)–O(2A)	93.5(3)	O(3′)–Cu(2)–O(1B)	94.3(3)	O(2)–Cu(3)–O(1C)	93.7(3)
O(2A)–Cu(1)–O(1A)	92.9(3)	O(1B)–Cu(2)–O(2B)	92.8(3)	O(1C)–Cu(3)–O(2C)	93.4(3)
O(1A)–Cu(1)–O(1)	94.3(3)	O(2B)–Cu(2)–O(3)	92.5(3)	O(2C)–Cu(3)–O(1)	93.9(3)
O(3′)–Cu(1)–O(1)	84.2(3)	O(1)–Cu(2)–O(3)	103.9(3)	O(1B)–Cu(3)–O(1)	79.0(3)
O(3′)–Cu(1)–O(2)	93.9(3)	O(1)–Cu(2)–O(3′)	84.4(3)	O(1B)–Cu(3)–O(2)	83.6(3)
O(3′)–Cu(1)–O(2A)	104.7(3)	O(1)–Cu(2)–O(1B)	87.7(3)	O(1B)–Cu(3)–O(1C)	100.3(3)
O(3′)–Cu(1)–O(1A)	91.3(3)	O(1)–Cu(2)–O(2B)	95.7(3)	O(1B)–Cu(3)–O(2C)	100.2(3)

(*b*) In the methoxo-group

O(1)–C(1)	1.432(11)	O(2)–C(2)	1.422(11)	O(3)–C(3)	1.427(11)
C(1)–O(1)–Cu(1)	124.0(6)	C(2)–O(2)–Cu(1)	128.6(6)	C(3)–O(3)–Cu(2)	123.2(6)
C(1)–O(1)–Cu(3)	119.9(6)	C(2)–O(2)–Cu(3)	128.2(6)	C(3)–O(3)–Cu(2′)	123.5(6)
C(1)–O(1)–Cu(2)	112.5(6)	Cu(1)–O(2)–Cu(3)	102.8(3)	C(3)–O(3)–Cu(1′)	106.0(6)
Cu(1)–O(1)–Cu(3)	98.9(3)			Cu(2)–O(3)–Cu(2′)	99.5(3)
Cu(1)–O(1)–Cu(2)	95.0(3)			Cu(2)–O(3)–Cu(1′)	103.8(3)
Cu(3)–O(1)–Cu(2)	101.8(3)			Cu(2′)–O(3)–Cu(1′)	96.3(3)

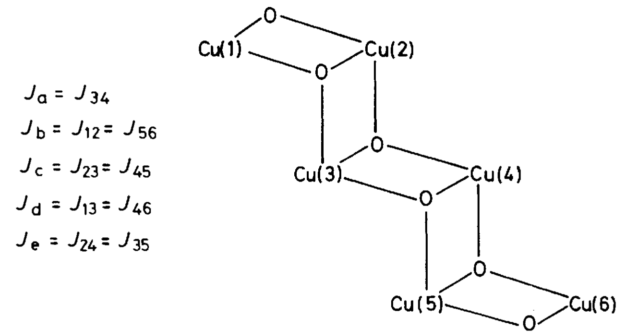
Symmetry code for primed atoms: $1 - x, \bar{y}, 1 - z$.

the copper(II) ions maintains their spin density in the dimer plane. There is no precedent for considerable interactions between the copper(II) ions of such geometry when linked through weak axial Cu–O bonds.

Theoretical considerations lead to the conclusion that for strictly square-pyramidal co-ordination of the copper(II) ions there are no such interactions.[14] In our case, neglect of interactions between the 'dimers' ($J_c = J_d = J_e = 0$) leads to a model of three non-interacting dimers and expression (2) for the

$$\chi = \frac{Ng^2\beta^2}{3kT}\left[\frac{1}{3 + \exp(-J_a/kT)} + \frac{2}{3 + \exp(-J_b/kT)}\right] + N\alpha \quad (2)$$

susceptibility (per mol Cu^{II}), where J_a = parameter for interactions in the inner 'dimer', J_b = parameter for interactions in the outer 'dimers', and the other symbols have their usual



meanings. $N\alpha$ was assumed to be equal to 0.75 mm^3 mol^{-1}. Equation (2) was fitted to the experimental data over the range 30—340 K using the minimum value of the standard deviation as a criterion for the best fit. The following values were obtained: $J_a = -214$ cm^{-1}, $J_b = -440$ cm^{-1}, and $g = 2.11$. Contour maps for the standard deviations of a broad range of parameters J_a, J_b, and g were also calculated. A correlation was found to exist between J_b and g, resulting in large uncertainties, which should be assigned to the best-fit values of these parameters. Assuming g to be fixed within the range 2.11 ± 0.05, in which the minimum value of the standard deviation is obtained (0.11 mm^3 mol^{-1}), gives the following uncertainties in the exchange parameters: $\Delta J_a = 2$ cm^{-1} and $\Delta J_b = 40$ cm^{-1}. Analysis of these maps also revealed the existence of another solution: $J_a = -514$ cm^{-1}, $J_b = -263$ cm^{-1}, and $g = 2.02$. However, in view of the higher value of the standard deviation (0.27 mm^3 mol^{-1}), this solution may be rejected. The present susceptibility data, contrary to previous results,[11] cannot be described by the HDvV model for a binuclear structure (Bleaney–Bowers equation). The excellent agreement between the susceptibilities measured and those calculated for the assumed model of three non-interacting dimers (Figure 3) confirms that this model is sufficient to describe our experimental data. Interactions between the dimeric units, if present, must influence the susceptibility data only to a minor degree.

The J_a and J_b parameters found characterize the exchange interactions in two molecularly different modifications of the same compound [$Cu_2(OMe)_2(tftbd)_2$]. Putting aside the effect of slight differences in distortion of the co-ordination of the copper(II) ions from ideal square-pyramidal co-ordination, the different geometries of the Cu_2O_2 bridging unit must be responsible for the significant differences found in the values of the above parameters. A stronger antiferromagnetic interaction ($J_b = -440$ cm^{-1}) occurs in the 'dimer' having the non-symmetric, slightly bent Cu_2O_2 ring with Cu–O–Cu bridging angles of 98.9(3) and 102.8(3)° (mean 100.5°), compared with the interaction ($J_a = -214$ cm^{-1}) found for the centrosymmetric 'dimer' with a bridge angle of 99.5(3)°. Undoubtedly, the bridge angles of the 'dimers' are an important factor in the observed differences in J. Available data for methoxo-bridged copper complexes are presented in Figure 4. It may be seen that a nearly linear relationship between J and the Cu–O–Cu bridging angle exists, but the slope is far higher than those for corresponding relationships found for hydroxo-bridged copper(II) dimers[9] and for the series of alkoxo-bridged compounds.[1] However, the present relationship, based on only four methoxo-compounds, requires confirmation by further studies. The structural origin of the large differences in J values is evidenced by the fact that the co-ordination around the methoxo-oxygen atoms of the centrosymmetric 'dimer' is tetrahedral, while one methoxo-oxygen atom in the non-symmetric dimer has planar co-ordination. The variation in dihedral angle between the carbon–oxygen bond of the alkoxo-group and the plane of the Cu_2O_2 ring has been suggested to have magnetic consequences[15] but the importance of this parameter is not known.

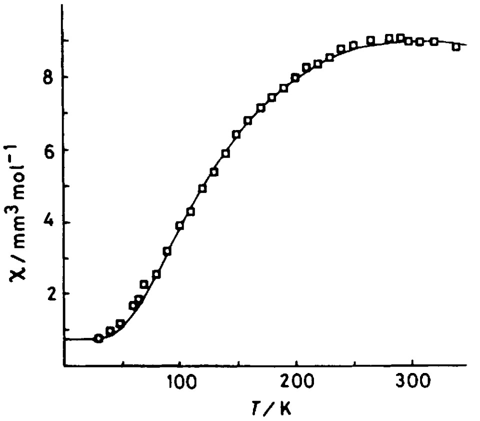


Figure 3. Temperature dependence of the magnetic susceptibility per mol Cu of [{$Cu_2(OMe)_2(tftbd)_2$}$_3$]. The solid curve is calculated from the model described in the text

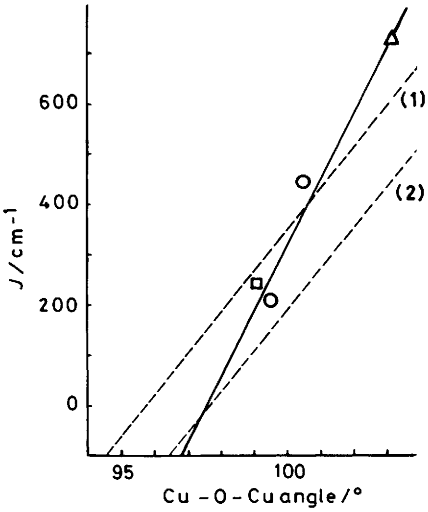


Figure 4. Relation between J and the Cu–O–Cu angle in methoxo-bridged copper complexes: [{$Cu_2(OMe)_2(tftbd)_2$}$_3$] (○), [{$Cu(OMe)(2,4,6\text{-}Cl_3C_6H_2O)(MeOH)$}$_4$] (□), and [$Cu_2(OMe)_2Cl_2(C_5H_5N)_2$] (Δ). The dashed lines represent the relationships found[1,9] for alkoxo-bridged (1) and hydroxo-bridged (2) copper complexes

Another meaningful comparison is between one of the methoxo-bridged 'dimers', reported herein, and the only known ethoxo-bridged complex,[5] [{$Cu_2(OEt)_2(tftbd)_2$}$_2$], containing nearly planar dimeric units with a Cu–O–Cu bridging angle of 99.8(3)°. The structural parameters in the ethoxo-bridged 'dimer' and the centrosymmetric methoxo-bridged 'dimer' are very similar, the bridging angles being the same (within experimental error) and the bridging oxygens in both 'dimers' having tetrahedral co-ordination. In spite of this structural similarity, the ethoxide 'dimer' exhibits a stronger interaction ($J = -352$ cm^{-1}) than the methoxide one ($J = -214$ cm^{-1}). However, it seems that the difference in J is too large to be attributed only to the difference in basicity of OEt and OMe.

Experimental

The complex was prepared as previously described[11] and recrystallized from acetone–methanol solution.

X-Ray Crystal Structure Determination.—*Crystal data.* $C_{54}H_{42}Cu_6F_{18}O_{18}S_6$, $M = 1\,894.5$, $a = 11.212(7)$, $b = 11.097(7)$, $c = 15.315(9)$ Å, $\alpha = 92.71(5)$, $\beta = 116.80(5)$, $\gamma = 95.56(5)°$, $U = 1\,681$ Å^3, D_m (by flotation) $= 1.88$ g cm^{-3}, $Z = 1$, $D_c = 1.87$ g cm^{-3}, $F(000) = 942$, space group $P\bar{1}$, Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu = 48.6$ cm^{-1}.

A prismatic crystal of dimensions *ca.* 0.25 × 0.1 × 0.1 mm was selected. Intensity data were recorded on a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Cu-K_α radiation. Intensities were measured using a 2θ–ω scan technique up to $2\theta = 114°$. The intensities of two standard reflections, monitored after every 50 intensity scans, showed no evidence of crystal decay. 4 016 Reflections were collected, of which 3 241 $[I > 3\sigma(I)]$ were used for the structure analysis. The data were corrected for background attenuation and Lorentz and polarization effects, only.

Structure determination and refinement. The structure was solved by use of MULTAN programs. The E map corresponding to the solution with the best figure of merit showed the Cu atoms and nine oxygen atoms. All other non-hydrogen atoms were found from Fourier difference maps. The H atoms from the methyl groups were found from difference synthesis. All the remaining H atoms were included in geometrically calculated positions with d(C–H) = 1.0 Å. Full-matrix least-squares refinements were carried out on the positional and anisotropic thermal parameters of all the non-hydrogen atoms. Least-squares refinement converged with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.058$ and $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.063$, where $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors were taken from ref. 16. The scattering factors for Cu, O, S, C, and F were corrected for real and imaginary components. All calculations were performed on a NOVA 1 200 computer with Syntex XTL/XTLE programs.[17] The thermal parameters for S(1) were rather high and too small for C(3A) suggesting that these atoms are mutually partially disordered by 180° rotation along the C(4A)–C(5A) bond. The final Fourier difference synthesis was featureless.

Magnetic Measurements.—Magnetic susceptibility data in the range 4.2—300 K were collected by the Faraday method using a Cahn electrobalance equipped with a digital voltmeter. The temperature was measured by a gold–iron/chromel thermocouple. A magnetic induction of 0.6 T was used. Data at temperatures above 300 K were obtained by the Gouy method. The salt Hg[Co(SCN)$_4$] was used as a susceptibility standard. All data were corrected for diamagnetism using Pascal's constants.

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