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

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The crystal and molecular structure of the title compound has been determined by a single-crystal *X*-ray diffraction study. The compound crystallizes in the space group *Fddd* of the orthorhombic system with eight tetrameric molecules in a cell of dimensions $a = 14.071(5)$, $b = 14.294(9)$, and $c = 49.93(3)$ Å. The structure has been refined to an *R* value of 0.076 for 1 354 independent reflections. The structure consists of D_2 symmetry tetranuclear molecules in which copper ions are linked by triply bridging OEt groups. The Cu_4O_4 core formed by copper atoms and ethoxy-oxygen atoms has a cubane-like structure: the Cu · · · Cu separations are 2.977(2), 3.260(2), and 3.281(2) Å, while the Cu–O bond lengths are 1.945(6), 1.947(6), and 2.411(7) Å; the Cu–O–Cu bridging angles are 99.8(3), 97.1(3), and 96.3(2)°. The co-ordination around each copper centre is roughly square-pyramidal. Magnetic susceptibility data (80—300 K) are interpreted in terms of the Heisenberg–Dirac–Van Vleck model. Substantial antiferromagnetic interactions ($2J = -352$ cm^{-1}) are found between copper ions in the roughly planar dimeric fragments of the tetranuclear molecule, and small interactions ($2J = -10$ cm^{-1}) between these fragments.

PREVIOUSLY we have reported [1] the preparation and physicochemical properties of several copper complexes of the general formula [CuL(OR)] (R = Me or Et, and L = various β-diketonate ligands). On the basis of magnetic and spectroscopic evidence we have assumed that these complexes are planar dimers with two alkoxy-bridges. A magnetic investigation of the compounds belonging to this series with other β-diketonate ligands has also been reported by other workers.[2,3]

All these compounds exhibit a temperature dependence of the magnetic moments with abnormally low values (0.7—1.4 B.M.) † at room temperature, which is evidence of antiferromagnetic interactions. Their magnetic behaviour is satisfactorily described by the isotropic Heisenberg–Dirac–Van Vleck model for a pair of interacting ions of $S = \frac{1}{2}$ (Bleaney–Bowers equation [4]). The structure of only one of these compounds, bis[di-μ-(benzyloxo)-bis(pentane-2,4-dionato)dicopper(II)] has been established.[5] This complex exists in a crystal as a tetrameric unit with the copper ions arranged at the parallelogram corners. The tetrameric molecule is built of two roughly planar alkoxy-bridged dimers held together by four axial copper–oxygen bonds. This structure, as well as the known propensity of the alkoxy-ligand to bridge more than two metal ions,[6-8] suggests that other members of the series might exhibit similar structural characteristics.

In this paper we report the details of a single-crystal *X*-ray diffraction study of another compound in the series with the formula [Cu(tftbd)(OEt)] [tftbd = 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate], performed to elucidate the molecular structure and to provide structural background for interpretation of the magnetic properties reported previously.[1] A preliminary communication of these results has been presented.[9]

EXPERIMENTAL

Preparation.—The preparation of the compound has been reported previously.[1] Crystals suitable for single-crystal *X*-ray study were obtained by dissolving the crude compound in benzene and setting aside for some weeks in a closed flask.

Crystal Data.—$C_{40}H_{36}Cu_4F_{12}O_{12}S_4$, Orthorhombic, $a = 14.071(5)$, $b = 14.294(9)$, $c = 49.93(3)$ Å, $D_m = 1.73$ g cm^{-3}, $Z = 8$, $D_c = 1.74$, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 4.35 mm^{-1}, space group *Fddd*. (Co-ordinates are in terms of an alternative unit cell in space group *Fddd* with origin on $\bar{1}$ at $\frac{1}{8},\frac{1}{8},\frac{1}{8}$ from 222.)

Intensity Measurements.—An irregularly shaped crystal with dimensions *ca.* 0.12 × 0.12 × 0.13 mm was selected for data collection. Intensity measurements were made on a Syntex $P2_1$ automatic diffractometer, by the θ—2θ scan method, and with graphite-monochromatized radiation. The total number of reflections, collected within $2\theta \leqslant 146°$, was 2 122. One standard reflection measured at regular intervals showed no evidence of crystal decay. Integral intensities were corrected for Lorentz and polarization factors; no absorption correction was applied. A final set of 1 354 independent non-zero reflections, with $I > 1.96\,\sigma(I)$, was used in the solution and refinement of the structure.

Determination and Refinement of the Structure.—The structure was solved with the MULTAN program of the '*X*-Ray' system (version of 1976). The solution was based on 183 reflections with $E \geqslant 1.5$ and $l_{max.} \leqslant 49$. The *E* map corresponding to the solution with the best figure of merit revealed the positions of 10 non-hydrogen atoms. The remaining non-hydrogen atoms were located from several Fourier and difference-Fourier syntheses. Full-matrix least-squares refinement, first with isotropic, then with anisotropic thermal parameters gave $R = 0.197$ and 0.081, respectively. Two H atoms from the methyl group were located from a difference-Fourier map. All remaining H atoms were placed in geometrically calculated positions (C–H 1.0 Å). Further refinement reduced *R* to 0.076. The final difference-Fourier synthesis was featureless.

All calculations except those of MULTAN were performed on a NOVA 1200 computer with programs supplied by Syntex. Neutral-atom scattering factors used were those listed in the International Tables.‡ No corrections for anomalous dispersion were made. Tables of observed and calculated structure factors and anisotropic temperature

† Throughout this paper: 1 B.M. ≈ 0.927 × 10^{-23} A m^2.

‡ 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

factors are available as Supplementary Publication No. SUP 22911 (24 pp.).†

RESULTS AND DISCUSSION

Description of the Structure.—The final atomic positional parameters are given in Table 1, the bond lengths and angles in Table 2.

The crystal structure of the title compound is composed of discrete tetranuclear molecules. The molecule, Figure 1, consists of the four formula units of [Cu(tftbd)-(OEt)] related by the crystallographic site symmetry 222, and joined together by the triply bridging oxygen atoms from the ethoxo-groups. The four copper ions

TABLE 1

Atomic positional parameters, with estimated standard deviations in parentheses. (Co-ordinates are in terms of an alternative unit cell in space group *Fddd* with origin on $\bar{1}$ at $\frac{1}{8},\frac{1}{8},\frac{1}{8}$ from 222)

Atom	*x*	*y*	*z*
Cu	0.199 2(1)	0.037 4(2)	0.103 76(3)
O(1)	0.188 3(4)	0.044 7(5)	0.142 55(11)
O(2)	0.191 0(5)	0.019 8(6)	0.065 41(11)
O(3)	0.335 3(5)	0.028 9(6)	0.103 65(13)
C(1)	0.253 0(8)	0.000 7(9)	0.161 05(17)
C(2)	0.244 7(10)	−0.102 5(9)	0.162 60(28)
C(3)	0.152 5(14)	−0.019 4(13)	−0.020 43(23)
C(4)	0.242 5(13)	−0.024 2(13)	−0.023 94(28)
C(5)	0.302 1(8)	−0.015 1(8)	−0.001 98(18)
C(6)	0.234 7(8)	−0.004 0(8)	0.021 09(19)
C(7)	0.260 6(8)	0.009 6(8)	0.049 39(18)
C(8)	0.354 9(8)	0.009 0(10)	0.056 58(20)
C(9)	0.385 7(7)	0.020 3(9)	0.082 68(21)
C(10)	0.491 6(11)	0.019 7(24)	0.087 48(30)
S	0.120 6(3)	−0.008 2(5)	0.012 18(7)
F(1)	0.543 8(5)	0.008 4(10)	0.067 62(16)
F(2)	0.517 8(8)	0.106 8(12)	0.092 99(28)
F(3)	0.518 0(6)	−0.018 7(15)	0.107 61(24)
H(11)	0.244	0.029	0.179 4
H(12)	0.321	0.016	0.155 0
H(21)	0.271	−0.125	0.145 8
H(22)	0.187	−0.125	0.166 7
H(23)	0.278	−0.128	0.179 3
H(3)	0.104	−0.024	−0.035 7
H(4)	0.270	−0.038	−0.043 5
H(5)	0.375	−0.016	−0.001 8
H(8)	0.405	0.000	0.042 0

of the tetrameric molecule are arranged as an irregular tetrahedron with Cu · · · Cu separations of 2.977(2), 3.260(2) and 3.281(2) Å, and together with the approximately tetrahedrally arranged bridging oxygen atoms form a cubane-like structure. A similar cubane structure has previously been described [10-13] for other copper tetramers. None of the six planes defining the ' cube ' is exactly planar. The deviations (Å) of the atoms from the respective mean planes are: 0.05 for the plane defined by Cu, Cu^{i}, O(1), O(1^{i}); 0.08 and 0.09 for the two remaining planes Cu, O(1), Cu^{ii}, O(1^{ii}) and Cu, O(1^{ii}), Cu^{iii}, O(1^{i}). The different intramolecular Cu · · · Cu separations and eight short Cu–O bonds and four longer ones indicate that the tetrameric unit can be thought of as two roughly planar ' dimers ' twisted one to another by 90° and associated by out of plane Cu–O bonds [2.411(7) Å] parallel to the *b* axis (Figure 1).

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2

Bond distances (Å) and angles (°) with standard deviations in parentheses

(*a*) In the co-ordination polyhedron *

Cu–O(1)	1.945(6)	Cu–O(2)	1.935(6)
Cu–O(1^{i})	1.947(6)	Cu–O(3)	1.919(6)
Cu–O(1^{ii})	2.411(7)		
O(1)–Cu–O(1^{i})	79.9(3)	O(2)–Cu–O(3)	92.8(3)
O(1)–Cu–O(2)	170.9(3)	O(1^{ii})–Cu–O(1)	82.3(3)
O(1)–Cu–O(3)	94.9(3)	O(1^{ii})–Cu–O(1^{i})	82.9(3)
O(1^{i})–Cu–O(2)	92.4(3)	O(1^{ii})–Cu–O(2)	101.6(3)
O(1^{i})–Cu–O(3)	174.7(3)	O(1^{ii})–Cu–O(3)	97.3(3)

(*b*) In the ethoxo-group *

O(1)–C(1)	1.441(12)	C(1)–C(2)	1.481(18)
C(1)–O(1)–Cu	124.4(6)	Cu–O(1)–Cu^{i}	99.8(3)
C(1)–O(1)–Cu^{i}	122.9(6)	Cu–O(1)–Cu^{ii}	97.1(3)
C(1)–O(1)–Cu^{ii}	110.2(6)	Cu^{i}–O(1)–Cu^{ii}	96.3(3)
O(1)–C(1)–C(2)	114.8(9)		

(*c*) In the tftbd ligand

O(2)–C(7)	1.273(12)	C(6)–C(7)	1.473(13)
O(3)–C(9)	1.271(12)	C(7)–C(8)	1.374(15)
S–C(3)	1.696(13)	C(8)–C(9)	1.383(14)
S–C(6)	1.667(11)	C(9)–C(10)	1.509(18)
C(3)–C(4)	1.281(25)	C(10)–F(1)	1.244(17)
C(4)–C(5)	1.386(18)	C(10)–F(2)	1.328(35)
C(5)–C(6)	1.500(14)	C(10)–F(3)	1.203(25)
Cu–O(2)–C(7)	126.2(7)	C(3)–C(4)–C(5)	119.0(16)
Cu–O(3)–C(9)	124.5(7)	C(4)–C(5)–C(6)	103.6(11)
O(2)–C(7)–C(8)	125.4(10)	C(5)–C(6)–C(7)	126.5(10)
O(2)–C(7)–C(6)	115.3(9)	C(6)–C(7)–C(8)	119.3(10)
O(3)–C(9)–C(8)	127.8(10)	C(7)–C(8)–C(9)	123.3(11)
O(3)–C(9)–C(10)	114.9(12)	C(8)–C(9)–C(10)	117.3(13)
S–C(6)–C(7)	120.0(8)	C(9)–C(10)–F(1)	117.2(18)
S–C(3)–C(4)	113.4(14)	C(9)–C(10)–F(2)	107.6(17)
S–C(6)–C(5)	113.6(8)	C(9)–C(10)–F(3)	116.1(19)
C(3)–S–C(6)	90.3(7)		

* Superscripts refer to atomic positions relative to atoms at *x*, *y*, *z* (no superscript): i $\frac{1}{4}-x, y, \frac{1}{4}-z$; ii $x, \frac{1}{4}-y, \frac{1}{4}-z$; iii $\frac{1}{4}-x, \frac{1}{4}-y, z$.

The two independent bridging Cu–O bond distances [1.945(6) and 1.947(6) Å] in the ' dimer ' are equal within experimental error showing that the Cu_2O_2 four-membered ring is almost symmetrical.

The co-ordination of the bridging oxygen atoms is roughly tetrahedral. The Cu–O(1)–C(1) angles are 124

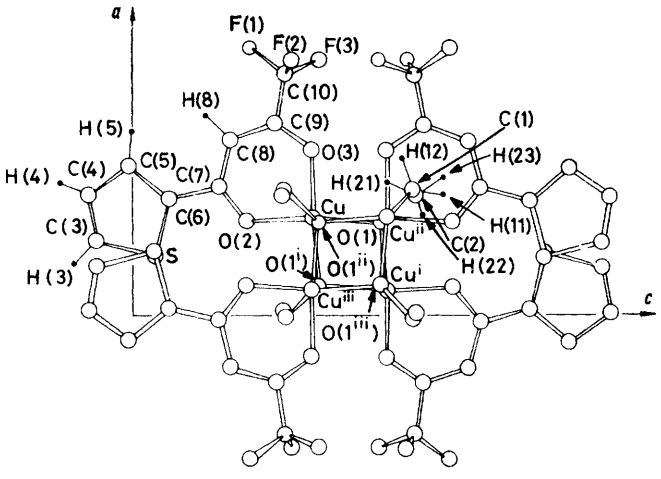

FIGURE 1 Projection of the molecular structure down the *b* axis

and 123° for copper atoms of the dimeric unit and 110° for a copper atom of the opposite dimer. The carbon atom bonded to each bridging oxygen deviates by *ca.* 0.58 Å from the mean plane of the Cu_2O_2 ring of the dimeric unit. This value is smaller than would be expected for tetrahedral geometry. The same value has also been found [14] for the doubly bridging alkoxy-groups.

The co-ordination of each copper atom is approximately square pyramidal. The four nearest oxygen atoms O(1), O(1^{i}), O(2), O(3) define the distorted basal plane; the oxygen atom O(1^{ii}) of another dimeric unit occupies the apex of the pyramid.

The distortion of the basal plane demonstrated by the twisting of the CuO_2 plane formed by the two ethoxy-oxygens with respect to the CuO_2 plane formed by two chelate oxygens is probably due to steric hindrance between the thienyl rings of the dimer units.

The observed bond distances and angles of the tftbd ligand are comparable to the values reported by other workers for metal complexes of this ligand.[15-18] For this reason they will not be considered here. Two of the carbon–fluorine distances have unreasonably short values. Similar erroneous values have been observed [19] in other structures containing CF_3 groups. In general the geometry of the chelate ring is close to that found as 'average' for the metal pentane-2,4-dionates by Lingafelter and Braun.[20] The calculations of the best planes showed that the C_3O_2 ligand skeleton and thienyl ring are planar within experimental error and approximately coplanar. The copper atom is not significantly displaced from the plane of the chelate ring.

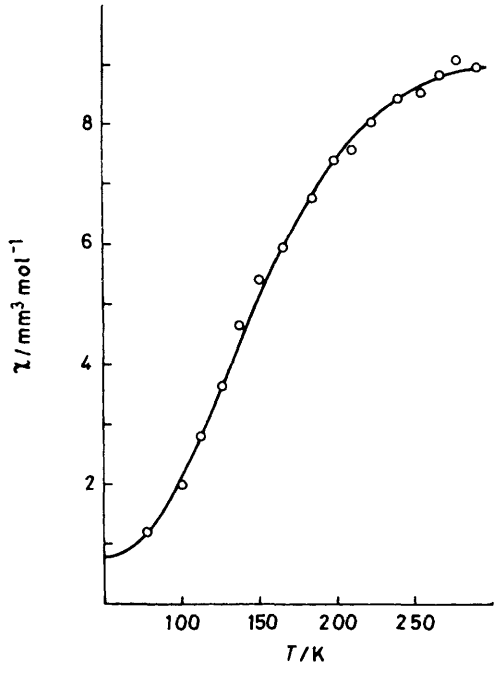

FIGURE 2 Temperature dependence of the magnetic susceptibility of [{Cu(tftbd)(OEt)}$_4$] per Cu atom. The solid curve is calculated from the tetramer model described in the text

Magnetism.—Magnetic properties of the compound [{Cu(tftbd)(OEt)}$_4$] are presented graphically in Figure 2. The shape of this curve and the temperature dependence of magnetic moments (0.15 and 1.24 B.M. at 78 and 295 K respectively) indicate that there are considerable copper–copper interactions in this complex.

In order to obtain information about the magnitude of exchange interaction between particular copper ions in the tetrameric molecule the experimental data were analyzed in terms of the isotropic Heisenberg–Dirac–Van Vleck approximation. The D_{2d} symmetry model, adequate for our tetramer, contains two independently variable exchange parameters: $J_{13} = J_{24} = J_a$; and $J_{12} = J_{14} = J_{23} = J_{34} = J_b$, where the subscripts refer to the individual copper ions numbered as shown in Figure 3. An analytical expression for the magnetic

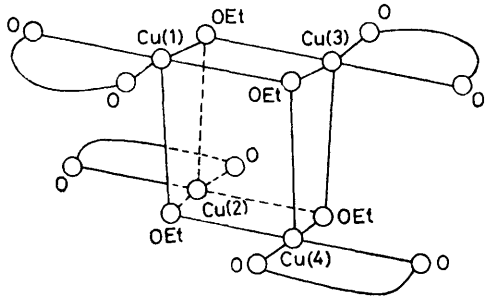

FIGURE 3 Schematic representation of the structure of [{Cu(tftbd)(OEt)}$_4$] with tftbd skeletons indicated by loops

susceptibilities of such a tetranuclear model has already been provided.[21] This expression was fitted by a least-squares procedure to the susceptibilities measured as a function of J_a and J_b. The standard deviation was used as the fitting criterion. The value of the temperature-independent paramagnetism, $N(\alpha)$, was fixed at 0.75 mm^3 mol^{-1}. The minimization procedure has been carried out for various fixed values of the g factor. It was found that the J_b parameter is very sensitive to the g value assumed (contrary to the J_a parameter and the closeness of the fit). The best-fit exchange parameters with g fixed at 2.10 are $2J_a = -352$ cm^{-1} and $2J_b = -10$ cm^{-1}. Since the e.s.r. spectrum of the compound is poorly resolved and only very broad lines could be observed at $g > 2$, the value $g = 2.10$ was assumed on the basis of e.s.r. data of closely related systems.[2a,3] Experimental magnetic data may be satisfactorily described also by the Bleaney–Bowers equation with the best-fit exchange parameter $2J = -354$ cm^{-1}, and fixed g and $N(\alpha)$ values as in the tetramer model. Standard deviations of the best-fit experimental data for the tetramer and dimer models are 0.14 and 0.15 mm^3 mol^{-1} respectively. These results are indicative of considerable antiferromagnetic interactions within the dimeric units, and small interactions between them. It should be noted that the precise value of the interdimer interaction cannot be determined from the present data.

The magnitudes of the exchange interactions between particular copper ions in the tetramer may be compared

with those found for copper(II) dimers. Structural and magnetic data are available for several copper dimers [22-24] in which a three-co-ordinated bridging oxygen links the apical co-ordination site of one of the square-pyramidal copper ions with the basal site of another copper ion. Hence, the Cu_2O_2 bridge lies in an approximately perpendicular plane to the molecular plane containing the unpaired electron bound to the square-pyramidally co-ordinated copper ion. The absence of any interaction or a triplet ground state found in these compounds is comparable with weak interactions between the dimeric units in our compound. Putting aside small distortions from the ideal square-pyramidal geometry at copper and the low non-planarity of the Cu_2O_2 bridge, the dimeric sub-molecule of our compound may be included among the class of dimers whose common property is the C_{4v} geometry at copper and a Cu_2O_2 bridge in the basal plane of both copper ions. This class of compounds includes hydroxo-bridged complexes for which Hatfield and co-workers [25] found a linear relationship between the singlet–triplet separation and Cu–O–Cu angle. The exchange parameter $|2J_a| = 352$ cm^{-1} for the dimeric unit of our compound is significantly higher than the value of *ca.* 180 cm^{-1} predicted by this relationship for the Cu–O–Cu angle of 99.8°.

The qualitative explanation for this difference may be connected with the different chemical nature of the bridging groups, *i.e.* the more basic character of OEt as compared to OH. The greater antiferromagnetic interaction in our compound in comparison to the hydroxo-bridged compounds is in agreement with the theoretical calculations of Hoffmann and co-workers,[26] which predict that for superexchange interaction an increase in the electron density on the bridging atoms enhances the antiferromagnetic coupling.

We thank Dr. A. Ożarowski for writing the computer program for least-squares fitting of magnetic susceptibility data and for computing.

[0/031 *Received*, 7th *January*, 1980]

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