Crystal structure, magnetic and spectroscopic properties of the bis(dimethyl sulfoxide) adduct of tetra-μ-formato-dicopper(II), a new tetracarboxylato-bridged copper(II) dimer

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Abstract

The crystal and molecular structure of a new tetracarboxylato-bridged copper(II) dimer, the bis(dimethyl sulfoxide)tetrakis(μ-formato)dicopper(II) has been determined by X-ray diffraction methods. It crystallizes in the tetragonal space group $I4_1/a$, with $Z=8$ in a cell of dimensions $a=17.688(2)$, $c=10.408(1)$ Å. The structure is built up of centrosymmetric neutral dimers $[Cu_2(HCOO)_4(dmso)_2]$, where four bidentate carboxylate anions form *syn–syn* bridges between the metal atoms which are in a 4+1 environment Magnetic susceptibility data show that the copper atoms are strongly antiferromagnetically coupled with $J=-434$ cm^{-1} The obtained triplet–singlet energy gap is compared with those reported for a series of related dimers. Finally, the ESR spectrum shows characteristic features of a triplet state with a non-negligible zero field splitting, being typical of the copper(II) dimeric tetracarboxylates

Key words: Crystal structures; Copper complexes; Carboxylato complexes; Dinuclear complexes

Introduction

Recently we undertook the study of two structural modifications of the anhydrous copper(II) formate which may be considered as very simple molecular magnets [1]. In that study, the β-$[Cu(HCOO)_2]$ phase was obtained for the first time by direct synthesis in solution. Until then, this phase had been exclusively prepared by topotactic dehydration of the copper(II) formate tetrahydrate, $Cu(HCOO)_2 \cdot 4H_2O$ [2]. This latter compound has a layered structure [3], and exhibits remarkable magnetic and electrical properties. Partial substitution of the water molecules by larger urea molecules led to the obtention of the compound $Cu(HCOO)_2 \cdot 2(NH_2)_2CO \cdot 2H_2O$, which still keeps the layered structure but not the antiferroelectric behaviour observed in the related tetrahydrate [4].

In order to further explore the chemical and structural factors governing both magnetic and electrical properties in these systems, we considered the preparation of compounds similar to the urea adduct, but with bulkier molecules, such as dimethyl sulfoxide (hereafter, dmso). However, a binuclear copper(II) compound with the well known copper(II) acetate hydrate structure [5] was obtained instead (see below). This new compound is not devoid of interest because, although a relatively vast number of dimeric copper(II) carboxylate monoadducts $[Cu_2(RCOO)_4L_2]$ have been structurally and/or magnetically characterized [6], only a very few examples of formate derivatives are known [7–9]. We report here the crystal and molecular structure and the magnetic properties of this new tetraformato-bridged copper(II) dimer.

Experimental

Preparation of $[Cu_2(HCOO)_4(dmso)_2]$

CuO (0.795 g, 0.01 mol) was dissolved in 50 ml of a 20:80 mixture of formic acid (85%) and water to

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give a blue solution After filtration, dimethylsulfoxide (50 ml) was added and the solution, which turned green, was allowed to stand at 5 °C. After several days, dark green crystals appeared, which were separated by filtration and washed with a 1:1 mixture of water–dmso. *Anal.* Found· C, 20.9; H, 3.6; Cu, 27 2. Calc. for $C_4H_8CuO_5S$: C, 20.7; H, 3.5; Cu, 27.4%.

Physical measurements

IR spectra (KBr pellets) were recorded on a Pye-Unicam SP 2000 spectrometer. Electronic spectra (diffuse reflectance) were registered using a Perkin-Elmer Lambda 9 UV/VIS/IR spectrophotometer. Polycrystalline powder ESR spectra were recorded on Bruker ER 200 D (X-band) and ESP 300 (Q-band) spectrometers, both equipped with a low temperature device. Magnetic susceptibility measurements were carried out on polycrystalline samples with a pendulum-type apparatus equipped with a nitrogen cryostat. The experimental susceptibilities were corrected both for the diamagnetic contributions using the Pascal constants [10], and for the temperature independent paramagnetism of the Cu(II) ion estimated to be 6×10^{-5} cm^3 mol^{-1} per copper(II) ion.

X-ray structure determination

Crystal data

A green crystal of $C_8H_{16}Cu_2O_{10}S_2$ having an oblique prism shape and approximate dimensions of $0.15\times0.30\times0.40$ mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda=0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $12<2\theta<27°$, measured by the computer controlled diagonal slit method of centring. A tetragonal cell was obtained with equivalent reflections conforming to 4/*m* symmetry. Cell parameters and calculated volume are: $a=17.688(2)$, $c=10.408(1)$ Å, $V=3256.5$ Å^3. For $Z=8$ and $FW=463.42$ g mol^{-1} the calculated density is 1.89 g cm^{-3}. From the systematic absences of: hkl:$h+k+l=2n$; $hk0$:h, $k=2n$; hhl:$l=2n$; $00l$: $l=4n$; the space group was determined to be $I4_1/a$.

Data collection and reduction

The data were collected at a temperature of 22 °C using the $\omega/2\theta$ scan technique [11]. The scan rate varied from 1 to 7°/min (in ω). Data were collected to a maximum 2θ of 55.0°. A total of 8129 reflections was collected ($\pm h$, $+k$, $+l$), corresponding to monoclinic symmetry and including possible systematic absences. As a check on crystal and electronic stability 3 representative reflections were measured every 60 min. The slope of the least-squares line through a plot of intensity versus time indicated a total loss in intensity of 1.8%. A linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.015 with an average value of 1.007. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 29 1 cm^{-1} for Mo Kα radiation. An empirical absorption correction based on a series of Ψ-scans was applied to the data. Relative transmission coefficients ranged from 0.793 to 0.998 with an average value of 0.917. Intensities of equivalent reflections were then averaged. 51 reflections were rejected from the averaging process because their intensities differed significantly from the average. The agreement factors for the averaging of the 2607 observed and accepted reflections were 2.1% based on intensity and 1.5% based on F_o

Structure solution and refinement

The structure was solved by direct methods (MULTAN 11/84) [12]. Copper atoms were initially found, and the remaining atoms were located in successive difference Fourier syntheses. All hydrogen atoms were located in difference Fourier syntheses and were added to the structure factor calculations but their positions and temperature factors were not refined. The structure was refined in full-matrix least-squares (based on F). Scattering factors were taken from Cromer and Waber [13]. Anomalous dispersion effects were included in F_c [14]; the values for f' and f'' were those of Cromer [13]. Only the 1231 reflections having $I>3\sigma(I)$ were used in the refinements The final cycle of refinement included 100 variable parameters and converged with unweighted and weighted agreement factors of: $R=\Sigma[|F_o-F_c|]/\Sigma|F_o|=0.021$ and $R_w=(\Sigma w(|F_o|-|F_c|)^2)/\Sigma[wF_o^2])^{1/2}=0.028$, where $w=4F_o^2/([\sigma(I)]^2+[0.04F_o^2]^2)$. The standard deviation of an observation of unit weight was 0.94. There were three correlation coefficients greater than 0.5 (the highest was only 0.59). The highest peak in the final difference Fourier had a height of 0.22 e/Å^3 with an estimated error [15] based on F of 0.09; the map was flat and featureless Plots of $w(|F_o|-|F_c|)$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using MolEN [16]. Atomic coordinates are listed in Table 1.

Results and discussion

Crystal structure

The structure of the title compound consists of a dimeric unit of copper atoms bridged by four $HCOO^-$

TABLE 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in $[Cu_2(HCOO)_4(dmso)_2]$

Atom	x/a	y/b	z/c	B (Å^2)
Cu	0.26039(2)	0.24676(2)	0.62342(2)	1.973(5)
S	0.33762(4)	0.31404(4)	0.37420(6)	3.57(1)
O	0.2911(1)	0.2479(1)	0.4225(2)	2.88(3)
O(1)	0.2254(1)	0.3531(1)	0.6267(2)	3.05(3)
O(2)	0.15435(9)	0.2129(1)	0.6161(2)	2.80(3)
O(3)	0.2902(1)	0.1416(1)	0.6595(2)	2.79(3)
O(4)	0.3623(1)	0.2818(1)	0.6711(2)	3.09(4)
C(1)	0.2081(1)	0.3851(1)	0.7294(2)	2.70(5)
C(2)	0.1174(1)	0.2048(1)	0.7169(3)	2.78(5)
C(3)	0.2731(2)	0.3793(2)	0.3074(3)	5.04(7)
C(4)	0.3788(2)	0.2819(2)	0.2271(3)	4.12(6)

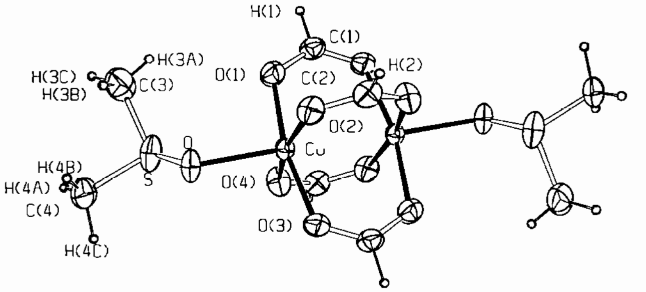

Fig. 1. ORTEP drawing of the $[Cu_2(HCOO)_4(dmso)_2]$ dimer showing 50% probability ellipsoids, including the atomic labelling scheme.

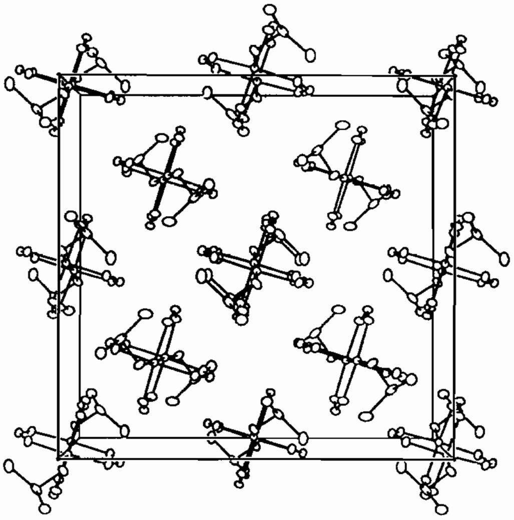

Fig. 2. View of the unit cell of $[Cu_2(HCOO)_4(dmso)_2]$.

ions; each copper is axially coordinated by a dmso molecule. Figure 1 presents an ORTEP drawing of the dimer and shows the $\bar{1}$ symmetry imposed on it. Figure 2 shows a unit cell view of the structure and the crystal packing allowed essentially by van der Waals forces. As usual in this kind of dimeric structures, four bidentate carboxylate anions form *syn–syn* bridges between the metal atoms which are in a 4+1 environment. The basal coordination of copper(II) ions is formed by four coplanar oxygen atoms from the bridging formate groups. The average Cu–O_{basal} distance (1.972(5) Å) falls in the range of values previously reported for analogous systems [5]. The apical position is occupied by the oxygen atom of a dmso molecule; this axial bond is *c.* 0.19 Å longer than the Cu–O_{basal} one (tetragonality parameter $T=0.91$). As expected, the copper atoms are shifted *c.* 0.21 Å out of the basal plane toward the dmso molecule.

The Cu–Cu separation (2.6629(4) Å) is very similar to the average value of the other three structurally characterized $[Cu_2(HCOO)_4L_2]$ compounds and slightly larger (about 0.05 Å) than that found for the cupric acetate monohydrate. With regard to the bond parameters of the tetraformate framework (see Table 2) they are close to those found in the dioxane and dithiocyanate adducts but differ significantly from that observed in the urea adduct. These structural parameters, besides the Cu–O_{ax} distance, are in acceptable agreement with the observed metal–metal separation according to the trends reported in the literature for tetracarboxylato-bridged metal dimers [17].

On the other hand, all relevant parameters for the dimethyl sulfoxide molecules are in good agreement with those previously reported for other dmso-containing complexes [18, 19].

Vibrational and electronic spectra

The IR spectrum of the title compound shows two strong absorption bands at 1580 and 1370 cm^{-1}, assigned to antisymmetric and symmetric carboxylate stretching

TABLE 2. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Cu coordination sphere			
Cu–O	2.161(2)	Cu–O(1)	1.980(2)
Cu–O(2)	1.970(2)	Cu–O(3)	1.969(2)
Cu–O(4)	1.969(2)		
O–Cu–O(1)	94.93(7)	O–Cu–O(2)	101.82(7)
O–Cu–O(3)	97.25(7)	O–Cu–O(4)	90.60(7)
O(1)–Cu–O(2)	89.52(7)	O(1)–Cu–O(3)	167.80(7)
O(1)–Cu–O(4)	89.02(8)	O(2)–Cu–O(3)	88.63(7)
O(2)–Cu–O(4)	167.58(7)	O(3)–Cu–O(4)	90.20(8)
Carboxylato bridges			
O(1)–C(1)	1.248(3)	O(2)–C(2)	1.244(3)
O(3)–C(1)	1.249(3)	O(4)–C(2)	1.243(3)
O(1)–C(1)–O(3)	128.0(2)	O(2)–C(2)–O(4)	128.1(2)
dmso molecule			
S–O	1.515(2)	S–C(3)	1.765(4)
S–C(4)	1.788(3)		
O–S–C(3)	106.5(1)	O–S–C(4)	105.0(1)
C(3)–S–C(4)	97.7(2)		

modes, respectively. In addition, another strong (and sharp) band is observed at 1020 cm^{-1} which is assigned to the S–O stretching mode of the dmso molecules, in agreement with their coordination to the copper(II) ions through the oxygen atom [20]

The diffuse reflectance spectrum is characterized by a very broad band in the visible region with a maximum at *c.* 14 000 cm^{-1}, which can be assigned, according to the literature [21], to unresolved d–d transitions in a C_{4v} symmetry Besides this, the spectrum displays two more intense bands centred at *c.* 27 000 and 40 000 cm^{-1}. In both cases, a charge-transfer assignment may be made, although the origin of the latter is controversial [6b, 22].

ESR spectroscopy

Both the X- and Q-band room-temperature ESR spectra of the studied compound exhibit broad features characteristic of a triplet state with a non-negligible zero field splitting. When the temperature is lowered the signals become sharper and their intensity decreases and ultimately vanishes below 77 K, when only sharp signals corresponding to diluted paramagnetic ($S = 1/2$) centres are observed. These results are in agreement with strong antiferromagnetic interactions in the copper(II) dimers.

The spectra can be analyzed with the spin Hamiltonian:

$$\mathcal{H} = \beta HgS + D[S_z^2 - 2/3] + E(S_x^2 - S_y^2)$$

In X-band, D is greater than the microwave energy and only three signals (Fig. 3) are observed, indicating moreover that $E \approx 0$, at

$$H_{\perp 2}^2 = (g_e/g_\perp)^2[H_0(H_0 + D')]$$

$$H_{z1} = (g_e/g_\parallel)(H_0 - D')$$

$$H_{z2} = (g_e/g_\parallel)(H_0 + D')$$

where $g_e = 2.0023$, $H_0 = h\nu/\beta g_e$ and $D' = D/\beta g_e$ [23]. From those expressions, the experimental field positions can be nicely reproduced with $g_\parallel = 2.37$, $g_\perp = 2.10$ ($g_{av} = 2.19$) and $D = 0.40$ cm^{-1}. However, in Q-band $D < h\nu$ (≈ 1.1 cm^{-1}) and five transitions are present (Fig. 3), three of them corresponding to $\Delta M_s = \pm 1$

$$H_{z1} = (g_e/g_\parallel)(H_0 - D')$$

$$H_{\perp 1}^2 = (g_e/g_\perp)^2[H_0(H_0 - D')]$$

$$H_{\perp 2}^2 = (g_e/g_\perp)^2[H_0(H_0 + D')]$$

and two of them to $\Delta M_s = \pm 2$; H_{min} characterizing the low-field limit of the spectrum and H_{dq} corresponding to a double quantum absorption [23]:

$$H_{min} = (g_e/g_{min})[(H_0^2/4 - D'^2/3)]^{1/2}$$

$$H_{dq} = (g_e/g_{av})[(H_0^2 - D'^2/3)]^{1/2}$$

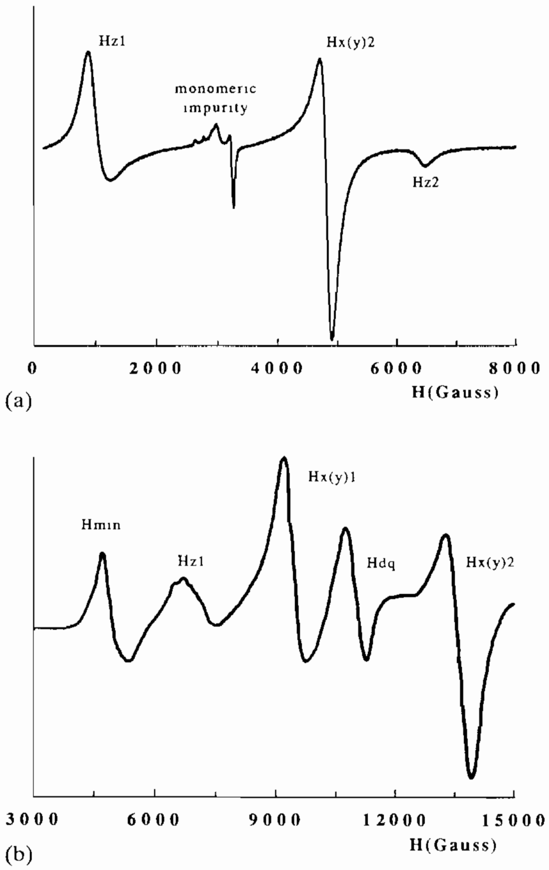

Fig 3 ESR spectra of [Cu$_2$(HCOO)$_4$(dmso)$_2$] at 180 K in X-band (a) and room temperature in Q-band (b)

Again, the positions of the experimental resonance fields can be reproduced with $g_\parallel = 2.34$, $g_\perp = 2.09$ ($g_{av} = 2.17$) and $D = 0.40$ cm^{-1} in full accordance with the X-band results. The values of g and D found are very similar to those observed for a large number of binuclear copper(II) carboxylate complexes.

Magnetic properties

The magnetic behaviour of the bis(dimethyl sulfoxide)tetrakis(μ-formato)dicopper(II) is illustrated in Fig 4 by means of a plot of $\chi_M T$ versus the temperature in the range 77–300 K. Upon cooling down from room temperature, the $\chi_M T$ product decreases continuously thus indicating a strong antiferromagnetic interaction between copper atoms in the dimers. The experimental data were fitted to the Bleaney-Bowers equation modified according to Kahn and co-workers [24] to take into account some paramagnetic impurity (ρ). The least-squares fitting procedure led to $J = -434$ cm^{-1}, $g = 2.16$ and $\rho = 0.01$. The absolute value obtained for the singlet–triplet energy gap is the lowest of those found for the structurally characterized tetraformate dicopper(II) derivatives, even though it is significantly larger

TABLE 3 Structural[a] and magnetic data for [$Cu_2(HCOO)_4L_2$] systems

L	Cu–Cu (Å)	Cu–O_{eq} (Å)	Cu–L (Å)	Cu–O–C (°)	C–O (Å)	O–C–O (°)	J (cm^{-1})	Reference
1/2 Dioxane	2.58(1)	1.96(2)	2.26(2)	113	1.24(4)	129.3(2)	−555	7
NCS^-	2.716(2)	1.983(4)	2.093(9)	122.7(3)	1.244(8)	128.4(5)	−485	8
Urea	2.657(7)	1.952(16)	2.114(13)	125.4(13)	1.27(2)	122.0(18)		9
Dmso	2.6629(4)	1.972(5)	2.161(2)	122.11(5)	1.246(3)	128.1(2)	−434	this work

[a]Mean values

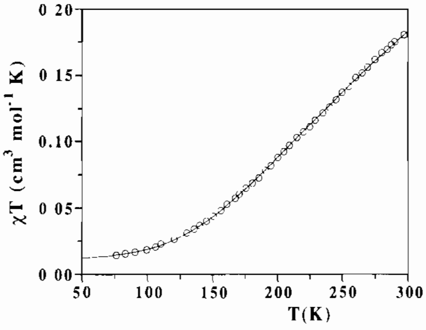

Fig. 4 Experimental $\chi_M T$ vs temperature for [$Cu_2(HCOO)_4(dmso)_2$] compound The solid line represents the least-squares fit (see text).

than those reported for the other tetra-μ-carboxylatodicopper(II) adducts (mean value about 300 cm^{-1}).

There have been several attempts to correlate the magnitude of J with structural parameters (related with the coordination sites and with the bridging groups) in the [$Cu_2(RCOO)_4$] cluster and/or with the donor properties of both carboxylate and axial ligands, but none of these efforts has proved successful [5a, 5b, 25]. In this sense, it must be pointed out that the estimated uncertainties in the J values (*c.* 5–10%, [26]) are of the same order of magnitude as the variations of that parameter within a series of related compounds (i.e. for the tetraacetato-dicopper(II) adducts the $|J|$ values fall in the range 285–325 cm^{-1} [5a, 5b, 25]). However, in the case of tetraformate derivatives the values of J span a much wider range (from −555 to −435 cm^{-1}) although unfortunately very few examples have been structurally and magnetically characterized. Thus the molecular structure and magnetic behaviour are known for only three adducts (including the title compound). An inspection of the structural parameters for these compounds (Table 3) indicates that, at first, no magneto-structural correlation can be established. In fact, some outstanding parameters involving the metal atoms such as the Cu–Cu or the Cu–O_{basal} distances and the C–O–Cu angle are not correlated with the copper(II)–copper(II) interaction. On the other hand, the structural differences in the bridging network are substantially within the experimental error.

With regard to theoretical considerations, Hoffman and co-workers [27] applied a molecular-orbital treatment focusing on the effect of the electron-withdrawing properties of the R group on the copper(II)–copper(II) interactions, but the results obtained did not agree too well with the experimental observations, especially for the formate derivative. Thus, the explanation of why the substitution of a more or less bulky R group for the hydrogen in [$Cu_2(RCOO)_4L_2$] dimers leads to a significant weakening of the coupling between copper ions, independently of the electron-withdrawing characteristics of R, is presently an open question.

Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles and observed and calculated structural factors can be obtained from the authors upon request.

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