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Spectroscopic, Magnetic and Structural Characterization of Bis(dimethyl sulfoxide)tetrakis(μ-2-nitrobenzoato-*O,O'*)dicopper(II)

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Abstract

The title compound, $Cu_2(2\text{-}NO_2C_6H_4COO)_4(DMSO)_2$, crystallizes in the monoclinic space group $P2_1/n$, with $a = 10.621(4)$, $b = 10.480(3)$, $c = 17.567(10)$ Å, $\beta = 96.15(8)°$. Single crystal X-ray data of 2534 independent reflections converged to a conventional R factor of 0.043. The complex has dimeric structure (copper acetate type), in which two copper(II) atoms are separated by 2.702(1) Å and bridged by four bidentate carboxylate groups with Cu–O (average) distance of 1.984(3) Å. The apical Cu–O bond to the DMSO molecule is 2.167(3) Å. There is a centre of symmetry at the middle of the Cu–Cu bond. Fitting of the modified Bleaney–Bowers equation to the magnetic susceptibility data yielded a singlet–triplet separation of $2J = -334$ cm^{-1}. The main properties of IR, EPR and electronic spectra at room temperature and the magnetic properties down to 4.2 K are reported.

Introduction

Although the literature on the structures of binuclear copper(II) carboxylates is fairly extensive [1], few aryl carboxylates have been subjected to full structural and magnetic characterization so that broader correlations between structural and magnetic parameters could be deduced. A recent article described the preparation, crystal structure and spectroscopic and magnetic characterization of a binuclear copper(II) benzoate with DMSO and summarized the spectral and magnetic data for binuclear copper(II) benzoates reported in the literature [2]. The 'windmill' cage or copper acetate type dimeric structure is commonly found for carboxylates, not only those of copper(II), but of chromium(II), molybdenum(II) and rhenium(II) ions as well [1, 3]. We now report the results of a structural, magnetic and spectroscopic characterization of copper(II) *ortho*-nitrobenzoate dimer with DMSO.

Experimental

Synthesis

Sodium salt of 2-nitrobenzoic acid was prepared from the acid (Fluka, puriss.) and NaOH (Merck, p.a.) using a small excess of acid to give a slightly acidic solution. A water solution of $CuSO_4 \cdot 5H_2O$ (Merck, p.a.) was added. The separated water adduct of copper(II) 2-nitrobenzoate was then dissolved in boiling DMSO with about 5–8% (volume) acetone to prevent the deterioration of the crude product. Well-developed, almost hexagonal plates were obtained after several days. The density of the crystals was 1.65 g cm^{-3} (flotation).

X-ray Structural Work

A crystal of 0.3 × 0.3 × 0.15 mm was selected for a single crystal structure determination. Cell parameters and the space group were determined from 15 well-centred independent reflections, after which the intensity data were immediately collected between $5° \leq 2\theta \leq 50°$ with varying scan rate from 2.5 to 29° min^{-1} at room temperature. Lorentz and polarization corrections were made in the usual manner but no absorption correction; $\mu(\text{Mo K}\alpha) = 12.8$ cm^{-1}. Three check reflections showed only statistical fluctuations during the data collection. A four-circle Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation was used. Altogether 2534 reflections with $F_o \geq 5\sigma(F_o)$ were included in the calculations.

Spectral Studies

Infrared spectra were measured on nujol mull (30–4000 cm^{-1}) and on KBr pellets (400–4000

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cm^{-1}) with a Perkin-Elmer spectrophotometer. The reflectance spectrum of the compound diluted in Li_2CO_3 (200–800 nm) was run on a Hitachi 356 spectrophotometer. Electron paramagnetic resonance spectra were obtained with an X-band Radiojon SE/X 2543 instrument for powdered samples at room and liquid nitrogen temperatures. A solid sample of Mn(II) in MgO was used as the reference and the magnetic field was calibrated with a nuclear magnetometer MJ 110R.

Magnetic Measurements

Magnetic susceptibility of a polycrystalline sample was measured by the Faraday method over the temperature range 4.2–290 K with a sensitive Cahn RG-HV electrobalance. The calibrant was $Hg[Co(SCN)_4]$, for which the magnetic susceptibility was taken as 16.44×10^{-6} cm^3 g^{-1} [4]. The correction for diamagnetism of the constituent atoms was calculated from Pascal's constants [5] and was -221×10^{-6} cm^3 mol^{-1}. The value of 60×10^{-6} cm^3 mol^{-1} was used as the t.i.p. per copper(II) atom. The magnetism of the sample was found to be field independent. See 'Supplementary Material'.

Crystal Data

$C_{32}H_{28}Cu_2N_4O_{18}S_2$, formula weight = 947.90, a = 10.621(4), b = 10.480(3), c = 17.567(10) Å, β = 96.15(8)°, V = 1944(1) $Å^3$, D_m = 1.65, D_c = 1.62 g cm^{-3}, Z = 2, $F(000)$ = 964, λ = 0.7107 Å, μ(Mo Kα) = 12.8 cm^{-1}, space group monoclinic $P2_1/n$ (no. 14).

Structure Determination

The copper atoms were localized from a three-dimensional Patterson map. Successive refinements and Fourier syntheses gave all the other non-hydrogen atoms, including the disordered sulphur atoms. Population parameters of 0.75 and 0.25 for sulphur S1 and S2, respectively, gave the best fit. In a final stage the H atoms (except for C17) were placed in their calculated positions and refined. The final R index was 0.043 (R_w = 0.041, weighting based on $1/\sigma^2(F_o)$) for 2534 reflections and 328 variables. Neutral atomic scattering factors were used in calculations. All calculations were done on a VAX 8650 computer using the XTAL program system [6]. The positions of the non-H atoms are listed in Table 1. See 'Supplementary Material'.

Results and Discussion

The crystal structure consists of centrosymmetric $Cu_2(2\text{-}NO_2C_6H_4COO)_4(DMSO)_2$ molecules (Fig. 1), where the centre of symmetry lies between the two copper(II) atoms. The copper(II) atoms are bridge-bonded by four *ortho*-nitrobenzoate anions as in

TABLE 1. The positional parameters and U_{eq} for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	a/x	b/y	c/z	U_{eq}
Cu	0.12172(4)	0.03144(4)	−0.00658(2)	0.02690(7)
C1	0.1050(4)	−0.0927(4)	0.2216(2)	0.0328(11)
C2	0.0444(4)	−0.0416(4)	0.2816(2)	0.0412(12)
C3	0.0575(5)	−0.0939(5)	0.3545(2)	0.055(2)
C4	0.1328(5)	−0.1995(5)	0.3689(2)	0.058(2)
C5	0.1982(5)	−0.2495(4)	0.3119(2)	0.0575(15)
C6	0.1845(4)	−0.1958(4)	0.2381(2)	0.0417(12)
C7	0.0739(4)	−0.0498(3)	0.1389(2)	0.0321(11)
C8	−0.0713(4)	0.3631(4)	0.0602(2)	0.0363(12)
C9	−0.1848(4)	0.4273(4)	0.0396(2)	0.0383(12)
C10	−0.2097(5)	0.5480(4)	0.0677(2)	0.0534(15)
C11	−0.1177(5)	0.6059(4)	0.1179(3)	0.059(2)
C12	−0.0060(5)	0.5448(4)	0.1398(3)	0.058(2)
C13	0.0199(5)	0.4246(4)	0.1116(3)	0.0491(14)
C14	−0.0456(4)	0.2273(3)	0.0356(2)	0.0322(11)
C15	0.5071(6)	0.1074(7)	−0.1120(4)	0.093(3)
C16[a]	0.3513(8)	−0.0916(7)	−0.1434(5)	0.093(3)
N1	−0.0294(4)	0.0782(4)	0.2684(2)	0.0609(13)
N2	−0.2829(3)	0.3729(3)	−0.0174(2)	0.0477(11)
O1	−0.0408(2)	−0.0648(2)	0.1129(1)	0.0361(8)
O2	0.1629(2)	−0.0139(2)	0.1029(1)	0.0339(7)
O3	0.0002(4)	0.1531(3)	0.2203(2)	0.0716(13)
O4	−0.1153(5)	0.0969(5)	0.3073(3)	0.120(2)
O5	0.0668(2)	0.2016(2)	0.0249(1)	0.0370(8)
O6	−0.1381(3)	0.1513(2)	0.0319(1)	0.0385(8)
O7	−0.2514(3)	0.3347(3)	−0.0777(2)	0.0614(11)
O8	−0.3928(3)	0.3752(4)	−0.0023(2)	0.0822(15)
O9	0.3084(3)	0.0804(3)	−0.0367(2)	0.0489(10)
S1[a]	0.3400(2)	0.0739(2)	−0.11806(9)	0.0565(6)
S2[b]	0.3936(5)	0.0016(5)	−0.0782(3)	0.059(2)
C17[b]	0.323(2)	−0.027(2)	−0.170(1)	0.063

[a] Population parameter 0.75. [b] Population parameter 0.25.

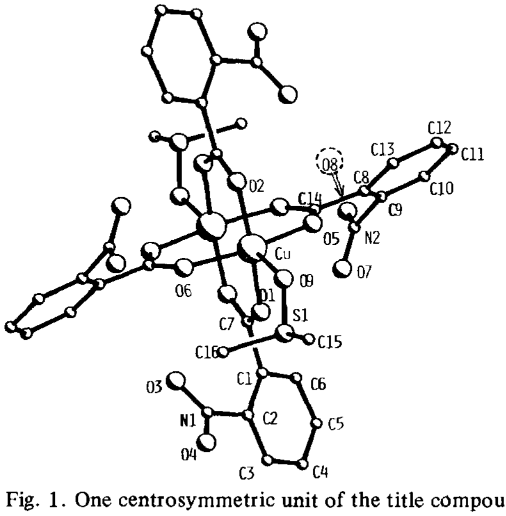

Fig. 1. One centrosymmetric unit of the title compound with atom labels.

TABLE 2. Selected bond lengths (Å)[a]

Cu–Cu*	2.702(1)	N1–C2	1.482(7)
Cu*–O1	2.002(3)	N1–O3	1.223(6)
Cu–O2	1.985(3)	N1–O4	1.218(7)
Cu–O5	1.970(3)	N2–C9	1.477(6)
Cu*–O6	1.980(3)	N2–O7	1.211(5)
Cu–O9	2.167(3)	N2–O8	1.226(6)
S1–O9	1.505(4)	C7–O1	1.270(5)
S1–C15	1.789(7)	C7–O2	1.245(5)
S1–C16	1.792(9)	C7–C1	1.525(6)
S2–O9	1.473(7)	C14–O5	1.266(6)
S2–C15	1.781(9)	C14–O6	1.261(5)
S2–C17	1.76(2)	C14–C8	1.513(6)

[a] In benzene rings the C–C bonds vary between 1.358(8)–1.410(7) Å with means 1.385 and 1.390 Å. *Denotes symmetry operation $-x, -y, -z$.

TABLE 3. Selected bond angles (°)[a]

Cu*–Cu–O9	170.8(1)	S1–O9–Cu	121.6(2)
O1*–Cu–O2	167.1(1)	S2–O9–Cu	127.9(3)
O5–Cu–O6*	166.9(1)	O9–S1–C15	105.0(3)
O1*–Cu–O9	92.4(1)	O9–S1–C16	108.3(4)
O2–Cu–O9	100.5(1)	C15–S1–C16	96.3(4)
O5–Cu–O9	99.1(1)	O9–S2–C15	106.9(4)
O6*–Cu–O9	94.0(1)	O9–S2–C17	108.2(8)
		C15–S2–C17	91.1(8)
Cu*–O1–C7	127.8(3)		
Cu–O2–C7	117.7(3)	O3–N1–O4	123.1(5)
O1–C7–O2	127.3(4)	O3–N1–C2	118.8(4)
O1–C7–C1	114.2(4)	O4–N1–C2	118.1(4)
O2–C7–C1	118.1(4)	O7–N2–O8	123.9(4)
		O7–N2–C9	118.5(4)
Cu–O5–C14	123.4(3)	O8–N2–C9	117.5(4)
Cu*–O6–C14	122.5(3)		
O5–C14–O6	126.9(4)		
O5–C14–C8	116.4(4)		
O6–C14–C8	116.6(4)		

[a] Asterisk denotes symmetry operation $-x, -y, -z$.

copper(II) acetate monohydrate. Each copper(II) atom shows a fivefold coordination in the form of a square pyramid, with four oxygen atoms of the bridging nitrobenzoate anions in the basal plane and one oxygen atom of a DMSO molecule at the apex. Selected bond lengths and angles are given in Tables 2 and 3. With a mean carboxylate Cu–O bond length of 1.984(3) Å, the square-pyramidal coordination entity CuO_5 is somewhat looser than that of the benzoate analogue [2] (mean bond length 1.96(1) Å). Also the copper–copper distance is longer: 2.702(1) Å, compared with 2.627(4) Å in the benzoate. The differences between the two compounds could be due to the more than 100 times weaker basicity of the *ortho*-nitrobenzoate than of the benzoate anion, with a resulting weaker coordination between the copper(II) atom and *ortho*-nitrobenzoate anion. The steric interaction between the COO^- and NOO groups could be another cause. The torsional angles between O2–C7–O1, O4–N1–O3, O6–C14–O5, O8–N2–O7 and the corresponding aromatic ring are 61.7(2), 28.9(2), 38.2(2) and 49.9(2)°, respectively. The sums of the torsional angles in the two nitrobenzoate anions are 90.6(2) and 88.1(2)°. As pointed out by Muhonen [7], the sum of the torsional angles is close to 90° in *ortho*-substituted nitrobenzoates generally.

The displacement of the copper(II) atoms from the basal plane towards the apical ligand, 0.225(2) Å, is greater than the displacements of 0.197 and 0.207 Å in the corresponding benzoate [2]. However, the apical Cu–O bonds to DMSO are almost identical (2.167(3)) Å with those of the benzoate (2.16 and 2.17 Å).

Selected structural parameters of the copper(II) arylcarboxylates (DMSO as apical ligand) are collected in Table 4. Statistically the sulphur atom of every fourth DMSO molecule is dissimilarly oriented in this work, with one methyl carbon C15 and the

TABLE 4. Some structural parameters of copper(II) arylcarboxylates when DMSO is the apical ligand. Distances in Å units

Compound (L = DMSO)	Cu–Cu	Cu–O (basal)	Cu–L (apical)	Cu–basal plane	$-2J$ (cm^{-1})	Reference
$Cu_2(2\text{-}NO_2C_6H_4COO)_4L_2$	2.702(1)	2.002(3) 1.985(3) 1.970(3) 1.980(3)	2.167(3)	0.225(2)	334	this work
$Cu_2(C_6H_5COO)_4L_2$	2.627(4)	1.96(1), 1.95(1) 1.93(1), 1.95(1) 1.97(1), 2.00(1) 1.99(1), 1.95(1)	2.16(1) 2.17(1)	0.197 0.207	304	2
$Cu_2(4\text{-}HOC_6H_4COO)_4L_6$	2.639(3)	1.95(1) 1.98(1) 1.96(1) 1.96(1)	2.12(1)	0.189(3)		8

oxygen retaining their positions and the sulphur S1 changing approximately to its mirror image S2 through the plane O9–C15–C16. Both the ordered and disordered DMSO molecules have bond length values typical for DMSO: S1–C15 1.789(7), S1–C16 1.792(9), S1–O9 1.505(4) Å and S2–C15 1.781(9), S2–C17 1.76(2), S2–O9 1.473(7) Å respectively. A similar disorder is found in $Cu_2(p\text{-}HOC_6H_4COO)_4(DMSO)_6$ [8], where the disordered sulphur atoms of the coordinated DMSOs are at a distance of 1.19(2) Å (1.14(1) Å in our compound).

The IR spectrum of $Cu_2(2\text{-}NO_2C_6H_4COO)_4(DMSO)_2$ shows a strong absorption band at about 1035 cm^{-1} which is attributed to the ν(SO) stretching of coordinated DMSO. The band is shifted to a lower wave number compared with the corresponding band of the free DMSO, ν(SO) 1055 cm^{-1} [9]. The carboxylate stretching frequencies, $\nu_{as}(COO^-)$ at 1645 cm^{-1} and $\nu_s(COO^-)$ at 1410 cm^{-1}, occur at similar energies to those reported for other copper(II) carboxylates having the dimeric copper(II) acetate structure [10, 11].

The electronic spectrum of the title compound shows a ligand field band with maximum at 1.34 μm^{-1} and shoulder at 2.80 μm^{-1}, which is typical for bridging systems with antiferromagnetic interactions [10, 12]. The position of the visible absorption band is shifted to longer wavelengths (lower energy) compared with $Cu_2(C_6H_5COO)_4(DMSO)_2$, which has a value of 1.40 μm^{-1} [2]. The shift is readily understandable from the X-ray structural properties of the CuO_5 chromophores: in the benzoate the five Cu–O bonds sum to 10.01(1) Å and in the nitrobenzoate to 10.105(3) Å.

The EPR powder spectrum of the complex exhibits an absorption band typical for the triplet state of axial symmetry and could be interpreted in terms of the effective spin Hamiltonian

$$\mathcal{H} = g\beta H\hat{S} + D\hat{S}_{z^2} + E(\hat{S}_{x^2} - \hat{S}_{y^2}) - (2/3)D$$

where D and E are the zero-field splitting parameters (axial and rhombic, respectively) and the other symbols have their usual meanings. The components of the triplet spectrum at room temperature appear at 670 G (H_{z_1}), 4730 G ($H_{\perp_2}$) and 6140 G (H_{z_2}) at $\nu = 9.235$ GHz. An additional line at 3135 G was assigned to the presence of a small monomer impurity of 1.28% calculated from the modified Bleaney–Bowers equation, $g_{imp} = 2.106$. For the triplet state spectrum we find $g_\perp = 2.089$, $g_\parallel = 2.412$, $g_{av} = 2.202$ and $|D| = 0.383$ cm^{-1}. A hyperfine pattern of seven lines of the parallel signals (H_{z_1} and H_{z_2}) and splitting of the perpendicular signal ($H_{\perp^2}$) into two components H_{x^2} (4620 G) and H_{y^2} (4720 G), ($E = 0.0017$ cm^{-1}) were observed at 77 K. The super-hyperfine lines in the low and high field regions show an average peak-to-peak widths of 64 and 63 G, respectively (see Fig. 2).

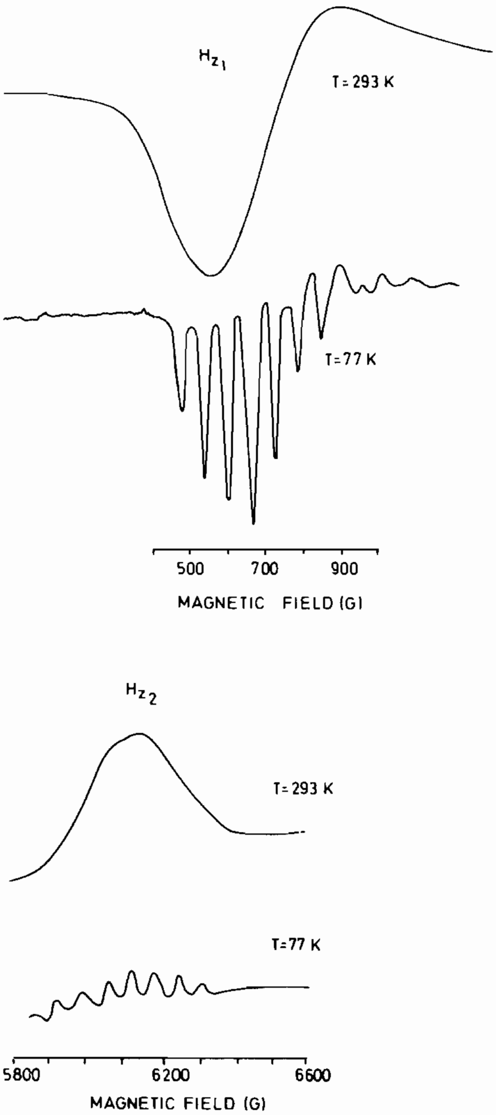

Fig. 2. The EPR powder spectrum at 77 and 293 K.

The title compound has a subnormal magnetic moment at room temperature, suggesting some coupling between the copper atoms. The magnetic susceptibility shows temperature dependence (Fig. 3) characteristic of the antiferromagnetic interaction of the two centres of the dimer. For an isotropic exchange interaction in a copper(II) dimer the Hamiltonian is $= -2JS_1S_2$, where J is the exchange parameter and S_1 and S_2 are the spin operators for the two copper(II) atoms. The value of the exchange parameter J was obtained from the modified Bleaney–Bowers equation

$$\chi_M{}^{corr} = N\beta^2 g_{av}{}^2(3kT)^{-1}(1 + 1/3(e^{-2J/kT}))^{-1}(1 - x)$$
$$+ (N\beta^2 g_{imp}{}^2)(4kT)^{-1}x$$

where x is the mole fraction of copper(II) atoms in

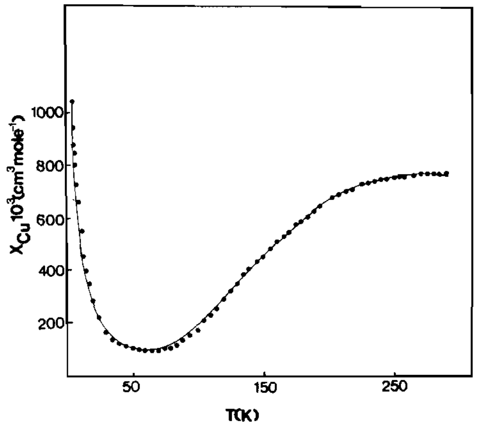

Fig. 3. In the magnetic susceptibility curve the experimental values are shown as circles and the theoretical values are represented by a solid line.

the monomeric form and the other symbols have their usual meanings. The spectroscopic splitting factors $g_{av} = 2.202$ (dimer) and $g_{imp} = 2.106$ (monomeric form) were obtained from the EPR spectrum and were not refined. The quality of the least-squares calculations was estimated from the residual function

$$f(X) = \sum_i (X_i(\text{calc}) - X_i(\text{exp}))^2$$

The best agreement of $f(X) = 1.6 \times 10^{-7}$ between the calculated susceptibilities (full line, Fig. 3) and experimental values (circles) was obtained, when $2J = 334$ cm^{-1} and the amount of monomeric impurity was 1.3%. The value obtained for $2J$ is typical for copper(II) carboxylate dimers [1].

Supplementary Material

The magnetic susceptibility data are obtainable from author J.M. on request. The list of structure factors is obtainable from author M.K. on request.

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