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Crystal Structure, Spectral and Magnetic Characterization of Bis(μ-benzoato–O, O′)(dimethylsulphoxide)copper(II)

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The crystal and molecular structure of the bis(μ-benzoato–O, O′) (dimethylsulphoxide) copper (II), $[Cu(C_6H_5COO)_2(DMSO)]_2$ (where DMSO is dimethylsulphoxide) were determined by the heavy-atom technique. The compound crystallizes in the monoclinic space group C2/c with four dimeric formula units in a cell with dimensions $a = 19.030(8)$ Å, $b = 15.494(9)$ Å, $c = 23.828(11)$ Å, and $\beta = 103.73(4)^\circ$. The observed and calculated densities are both 1.49 g cm^{-3}. The structure was refined by full-matrix least-squares methods to a final value of the R factor of 0.071, based on 1892 independent data with $I \geqslant 1.96\ \sigma(I)$. The compound is dimeric, with square pyramidal geometry at each copper center. Two copper atoms bridged by four carboxylate groups while the apical ligand is DMSO. The Cu····Cu distance is 2.627(3) Å. The Cu atoms are displaced by 0.197 Å (Cu_1) and 0.207 Å (Cu_2) from the plane containing four oxygen atoms towards the ligands DMSO. The magnetic susceptibility of the compound was measured as a function of temperature, and the data fitted to a Bleanay–Bowers equation which yields a singlet-triplet separation of 304 cm^{-1}. The EPR spectrum of the powdered solid is consistent with a spin of $S = 1$. The data are compared with those found in similar copper(II) benzoates.

While the literature on the structure of binuclear copper(II) carboxylates is considerable [1], a relatively small number of benzoate compounds have been the subject of structural characterization. The square pyramidal geometry, as defined in binuclear $Cu(C_6H_5COO)_2(C_4H_8O_2)_{2.5}$ [2], has a Cu–Cu distance of 2.569(3) Å. This distance is longer 2.606(3) Å in $Cu(C_6H_5COO)_2(CH_3OH)_2$ [3], 2.671(2) Å in $Cu(C_6H_5COO)_2C_9H_7N$ [4] and 2.681(1) Å in $Cu(C_6H_5COO)_2C_5H_5N$ [5], indicating that this distance is sensitive to molecule ligands coordinated in the axial position.

In this paper we describe the crystal structure determination, spectral and magnetic behaviours of the binuclear compounds formed between copper(II) benzoate and dimethylsulphoxide, in comparison with those found in familiar copper(II) benzoates.

Experimental

Copper(II) benzoate trihydrate [6] was dehydrated in air at 383 K for 1 hr. Anhydrous copper(II) benzoate was dissolved in dimethylsulphoxide at boiling point. Separation of the crude product from the concentrated solution by filtration, followed by recrystallization from dimethylsulphoxide, yielded dark-green well-developed crystals of the title compound. Calcd. for $Cu(C_6H_5COO)_2DMSO$, (DMSO = dimethylsulphoxide): C, 43.80; H = 4.20; Cu, 16.55. Found: C, 43.7; H, 4.16; Cu, 16.52.

The electronic spectrum in the region 1.0–2.8 μm^{-1} was measured with a Perkin-Elmer 450 spectrophotometer, and the infrared spectrum in the region 400–3600 cm^{-1} with the UR 10 spectrophotometer. In both cases the Nujol suspension technique was used. The EPR spectrum of the polycrystalline sample was measured at room temperature on a Varian E 4 spectrometer. Magnetic measurements were carried out at the University of Helsinki as previously described [7].

X-ray crystallographic measurements of the title compound were taken at room temperature. Cell parameters and the space group for the crystal were determined from the Weissenberg photographs and then refined from four position angles of 11 independent reflections. Intensity data were collected on a Syntex P2$_1$ diffractometer using graphite monochromated MoK$_{\bar{\alpha}}$ radiation.

A tetragonal prism crystal with dimensions of 0.23 × 0.23 × 0.19 mm was used for X-ray diffraction measurements. The 3206 intensities in the range $0 < 2\theta < 40^\circ$ were measured and corrected for Lorentz polarization effects and absorption. The

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$\theta - 2\theta$ scan technique with a variable scan rate of 4.88–29.3° min^{-1} and the scanning range from $2\theta(\mathrm{MoK}_{\alpha_1}) - 1°$ to $2\theta(\mathrm{MoK}_{\alpha_2}) + 1°$ were used. Two selected diffractions were monitored as standards after every 97 intensities, and recentering subroutines were made after every 500 intensity measurements. The final refinement of structure parameters was based on the 1892 intensities which had $F_o \geqslant 3.92\,\sigma(F_o)$. To calculate the absorption factor, experimental absorption curves for 7 diffractions with $2\theta = 7.75$, 11.75, 14.60, 18.52, 22.44, 26.94, and 30.11° were measured.

Crystal Data

$Cu_2C_{32}H_{32}O_{10}S_2$, M = 767.8; monoclinic, $a = 19.030(8)$, $b = 15.494(9)$, $c = 23.828(11)$ Å, $\beta = 103.73(4)°$, $V = 6825(6)$ Å^3, $D_m = 1.49$ g cm^{-3}, $Z = 8$, $D_c = 1.49$ g cm^{-3}, $F_{000} = 3152$, MoK$_{\bar{\alpha}}$ radiation, $\lambda = 0.7107$ Å; $\mu(\mathrm{MoK}_{\bar{\alpha}}) = 14.7$ cm^{-1}. Space group C2/c (C^6_{2h}, no. 15) [8].

Determination and Refinement of the Structure

The structure was determined by the heavy-atom technique. Isotropic full-matrix least-squares refinement of non-hydrogen atoms yielded $R_1 = 0.099$. Introduction of anisotropic thermal parameters for all non-hydrogen atoms gave final R-factors $R_1 = 0.092$ and $R_2 = 0.074$, where R_2 is weighted R-factor with $1/\sigma^2$ weight. In the last cycle of refinement the ratio shift/e.s.d. < 0.33 for each parameter. The maximum electron density in the corresponding difference Fourier synthesis was 0.96 e Å^{-3}.

On this stage of structure solution the positions of hydrogen atoms were computed using the HPOSN program [9]. The distances and angles for the computation of all the hydrogen atoms of the benzene ring were 1.06 Å and 120° respectively. The position of one of the hydrogen atoms from each methyl group of the DMSO molecule was determined from the foregoing difference Fourier synthesis (Table I); all other positions were computed for the interatomic distance (C–H) of 1.08 Å and the angle (H–C–H) of 109°. A comparison with the difference Fourier synthesis showed that in the obtained positions there was the maximum electron density.

The hydrogen atom positions obtained were not refined; they were however used for the computation of the structure factor value. The value of the respective coefficient of the isotropic temperature factor was higher by one unit than that of the carbon atom to which the given hydrogen atom was bonded. The final value of R_2 was 0.071, while the residual electron density in the final difference Fourier synthesis had a value of 0.77 e Å^{-3}. Final atomic positional and thermal parameters are given in Table II.

The structure calculations were carried out on an XTL-system [9] and on a Siemens 4004/150 system

TABLE I. Positional Parameters for Hydrogen Atoms Localized from Difference Fourier Synthesis.

Atom	x	y	z	B_{iso}
H(512)	0.03570	−0.02210	0.15020	6.54
H(521)	0.0100	−0.2250	0.1800	5.07
H(612)	0.25750	0.39270	0.20080	5.63
H(622)	0.26040	0.37780	0.04470	5.98

TABLE II. Positional Parameters with E.S.D.s in Parentheses.

Atom	x	y	z
Cu(1)	0.2113(1)	−0.0064(1)	0.1590(1)
Cu(2)	0.2793(1)	0.1410(1)	0.1586(1)
S(1)	0.1030(3)	−0.1336(3)	0.2018(2)
S(2)	0.3294(3)	0.3445(3)	0.1391(2)
O(1)	0.2482(6)	−0.0320(6)	0.0909(4)
O(2)	0.2994(6)	−0.0491(6)	0.2088(4)
O(3)	0.1297(5)	0.0543(6)	0.1082(5)
O(4)	0.1837(6)	0.0475(7)	0.2266(5)
O(5)	0.1519(6)	−0.1241(7)	0.1628(5)
O(6)	0.3112(5)	0.0909(6)	0.0940(4)
O(7)	0.3537(5)	0.0803(6)	0.2149(4)
O(8)	0.1880(6)	0.1774(6)	0.1025(4)
O(9)	0.2359(6)	0.1733(6)	0.2217(5)
O(10)	0.3450(6)	0.2566(6)	0.1641(4)
C(10)	0.1341(8)	0.1304(10)	0.0908(7)
C(11)	0.0664(8)	0.1616(9)	0.0494(6)
C(12)	0.0095(9)	0.1048(10)	0.0276(7)
C(13)	−0.0510(9)	0.1329(11)	−0.0111(7)
C(14)	−0.0584(9)	0.2172(11)	−0.0288(7)
C(15)	−0.0020(11)	0.2722(11)	0.0093(8)
C(16)	0.0612(9)	0.2469(10)	0.0317(8)
C(20)	0.2008(7)	0.1230(9)	0.2438(6)
C(21)	0.1765(8)	0.1543(9)	0.2953(6)
C(22)	0.1310(11)	0.1019(12)	0.3188(8)
C(23)	0.1098(11)	0.1291(11)	0.3679(8)
C(24)	0.1288(11)	0.2078(11)	0.3902(8)
C(25)	0.1732(11)	0.2607(12)	0.3675(8)
C(26)	0.1963(9)	0.2338(9)	0.3201(7)
C(30)	0.3510(7)	0.0004(11)	0.2310(6)
C(31)	0.4118(8)	−0.0307(9)	0.2778(6)
C(32)	0.4145(9)	−0.1183(10)	0.2913(7)
C(33)	0.4702(10)	−0.1496(11)	0.3369(9)
C(34)	0.5208(9)	−0.0926(12)	0.3667(8)
C(35)	0.5183(8)	−0.0061(12)	0.3509(6)
C(36)	0.4647(7)	0.0233(11)	0.3075(7)
C(40)	0.2897(8)	0.0189(9)	0.0723(6)
C(41)	0.3159(8)	−0.0113(9)	0.0207(6)
C(42)	0.2853(8)	−0.0831(11)	−0.0096(7)
C(43)	0.3088(9)	−0.1075(12)	−0.0570(8)
C(44)	0.3609(11)	−0.0594(11)	0.0744(7)
C(45)	0.3967(9)	0.0114(11)	−0.0428(7)
C(46)	0.3709(8)	0.0353(10)	0.0038(7)
C(51)	0.0245(11)	−0.0863(18)	0.1659(11)
C(52)	0.0722(12)	−0.2416(12)	0.1930(8)
C(61)	0.2484(12)	0.3796(13)	0.1558(11)
C(62)	0.2976(13)	0.3282(15)	0.0643(9)

using NCR crystallographic programs by Ahmed [10] for final block-diagonal least-squares refinement of 415 parameters. The atomic scattering factors were included from ref. [11]. Bond distances and angles are listed in Table III.

TABLE III. Bond Distances (Å) and Angles (°) (not Involving Hydrogen Atoms) with Their Estimated Standard Deviations.

(a) In the co-ordination sphere of the copper(II) atoms			
Cu(1)–Cu(2)	2.627(2)		
Cu(1)–O(1)	1.96(1)	Cu(2)–O(6)	1.95(1)
Cu(1)–O(2)	1.93(1)	Cu(2)–O(7)	1.95(1)
Cu(1)–O(3)	1.97(1)	Cu(2)–O(8)	2.00(1)
Cu(1)–O(4)	1.99(1)	Cu(2)–O(9)	1.95(1)
Cu(1)–O(5)	2.16(1)	Cu(2)–O(10)	2.17(1)
O(1)–Cu(1)–O(2)	90.6(4)	O(6)–Cu(2)–O(7)	92.2(4)
O(1)–Cu(1)–O(3)	88.5(4)	O(6)–Cu(2)–O(8)	88.2(4)
O(1)–Cu(1)–O(4)	166.2(4)	O(6)–Cu(2)–O(9)	169.7(4)
O(1)–Cu(1)–O(5)	99.1(4)	O(6)–Cu(2)–O(10)	95.4(4)
O(2)–Cu(1)–O(3)	171.0(4)	O(7)–Cu(2)–O(8)	165.7(4)
O(2)–Cu(1)–O(4)	90.2(4)	O(7)–Cu(2)–O(9)	88.0(4)
O(2)–Cu(1)–O(5)	94.1(4)	O(7)–Cu(2)–O(10)	92.4(4)
O(3)–Cu(1)–O(4)	88.6(4)	O(8)–Cu(2)–O(9)	89.1(4)
O(3)–Cu(1)–O(5)	94.9(4)	O(8)–Cu(2)–O(10)	101.8(4)
O(4)–Cu(1)–O(5)	94.6(4)	O(9)–Cu(2)–O(10)	95.0(4)
Cu(2)–Cu(1)–O(1)	84.2(3)	Cu(1)–Cu(2)–O(6)	84.4(3)
Cu(2)–Cu(1)–O(2)	86.8(3)	Cu(1)–Cu(2)–O(7)	81.7(3)
Cu(2)–Cu(1)–O(3)	84.2(3)	Cu(1)–Cu(2)–O(8)	84.1(3)
Cu(2)–Cu(1)–O(4)	82.1(3)	Cu(1)–Cu(2)–O(9)	85.4(3)
Cu(2)–Cu(1)–O(5)	176.6(3)	Cu(1)–Cu(2)–O(10)	174.1(3)
Cu(1)–O(1)–C(40)	123(1)	Cu(2)–O(6)–C(40)	123(1)
Cu(1)–O(2)–C(30)	122(1)	Cu(2)–O(7)–C(30)	126(1)
Cu(1)–O(3)–C(10)	123(1)	Cu(2)–O(8)–C(10)	122(1)
Cu(1)–O(4)–C(20)	124(1)	Cu(2)–O(9)–C(20)	123(1)
(b) In the carboxylate groups			
C(10)–O(3)	1.26(2)	C(30)–O(2)	1.26(2)
C(10)–O(8)	1.23(2)	C(30)–O(7)	1.30(2)
C(20)–O(4)	1.26(2)	C(40)–O(1)	1.27(2)
C(20)–O(9)	1.22(2)	C(40)–O(6)	1.26(2)
O(3)–C(10)–O(8)	126(1)	O(2)–C(30)–O(7)	122(1)
O(3)–C(10)–C(11)	113(1)	O(2)–C(30)–C(31)	121(1)
O(8)–C(10)–C(11)	120(1)	O(7)–C(30)–C(31)	117(1)
O(4)–C(20)–O(9)	125(1)	O(1)–C(40)–O(6)	125(1)
O(4)–C(20)–C(21)	118(1)	O(1)–C(40)–C(41)	117(1)
O(9)–C(20)–C(21)	117(1)	O(6)–C(40)–C(41)	118(1)
(c) In the phenyl rings			
C(11)–C(12)	1.39(2)	C(31)–C(32)	1.39(2)
C(12)–C(13)	1.36(2)	C(32)–C(33)	1.41(3)
C(13)–C(14)	1.37(2)	C(33)–C(34)	1.37(3)
C(14)–C(15)	1.36(3)	C(34)–C(35)	1.39(3)
C(15)–C(16)	1.41(3)	C(35)–C(36)	1.35(2)
C(16)–C(11)	1.39(2)	C(36)–C(31)	1.37(2)
C(11)–C(10)	1.50(2)	C(31)–C(30)	1.48(2)
C(21)–C(22)	1.40(3)	C(41)–C(42)	1.38(2)
C(22)–C(23)	1.39(3)	C(42)–C(43)	1.36(2)
C(23)–C(24)	1.35(2)	C(43)–C(44)	1.38(3)
C(24)–C(25)	1.38(3)	C(44)–C(45)	1.41(2)
C(25)–C(26)	1.37(2)	C(45)–C(46)	1.36(2)
C(26)–C(21)	1.38(2)	C(46)–C(41)	1.41(2)
C(21)–C(20)	1.49(2)	C(41)–C(40)	1.51(2)
C(10)–C(11)–C(12)	121(1)	C(30)–C(31)–C(32)	118(1)
C(11)–C(12)–C(13)	121(2)	C(31)–C(32)–C(33)	119(2)
C(12)–C(13)–C(14)	121(2)	C(32)–C(33)–C(34)	119(2)
C(13)–C(14)–C(15)	118(2)	C(33)–C(34)–C(35)	120(2)
C(14)–C(15)–C(16)	122(2)	C(34)–C(35)–C(36)	120(2)
C(15)–C(16)–C(11)	118(2)	C(35)–C(36)–C(31)	121(1)
C(16)–C(11)–C(12)	119(1)	C(36)–C(31)–C(32)	120(1)
C(10)–C(11)–C(16)	119(1)	C(30)–C(31)–C(36)	122(1)
C(20)–C(21)–C(22)	119(1)	C(40)–C(41)–C(42)	120(1)
C(31)–C(22)–C(23)	120(2)	C(41)–C(42)–C(43)	118(2)
C(22)–C(23)–C(24)	120(2)	C(42)–C(43)–C(44)	120(2)
C(23)–C(24)–C(25)	121(2)	C(43)–C(44)–C(45)	123(2)
C(24)–C(25)–C(26)	119(2)	C(44)–C(45)–C(46)	115(2)
C(25)–C(26)–C(11)	121(2)	C(45)–C(46)–C(41)	122(1)
C(26)–C(21)–C(22)	119(1)	C(46)–C(41)–C(42)	121(1)
C(20)–C(21)–C(26)	122(1)	C(40)–C(41)–C(46)	119(1)
(d) In the dimethylsulphoxide molecules			
S(1)–O(5)	1.47(1)	S(2)–O(10)	1.49(1)
S(1)–C(51)	1.70(3)	S(2)–C(61)	1.77(2)
S(1)–C(52)	1.77(2)	S(2)–C(62)	1.76(2)
Cu(1)–O(5)–S(1)	121.8(6)	Cu(2)–O(10)–S(2)	132.3(6)
O(5)–S(1)–C(51)	104(1)	O(10)–S(2)–C(61)	107.1(9)
O(5)–S(1)–C(52)	105.2(8)	O(10)–S(2)–C(62)	105.2(9)
C(51)–S(1)–C(52)	97(1)	C(61)–S(2)–C(62)	99(1)

Results and Discussion

A drawing of the crystal structure of $[Cu(C_6H_5COO)_2DMSO]_2$ viewed along the orthogonal (010) projection of the molecule is shown in Fig. 1. The compound exists as a dimer consisting of two distorted square-based pyramidal copper(II) polyhedra joined by four carboxylic groups of benzoate ions with a dimethylsulphoxide molecule coordinated through the oxygen atom at each apex at the distance of 2.16(1) Å for Cu 1 and 2.17(1) Å for Cu 2. The bridge, similar structurally to that found in copper(II) acetate, is required by crystallographic symmetry to be almost planar and contains crystallographically non-equivalent Cu–O bond distances and bond angles (Table III). The copper atoms are 0.197 Å (Cu 1) and 0.207 Å (Cu 2) above their basal planes toward the apical oxygen atoms. The displacement of the copper atom from the basal plane toward the apical ligand is in agreement with that found in most square pyramidal copper(II) compounds [1].

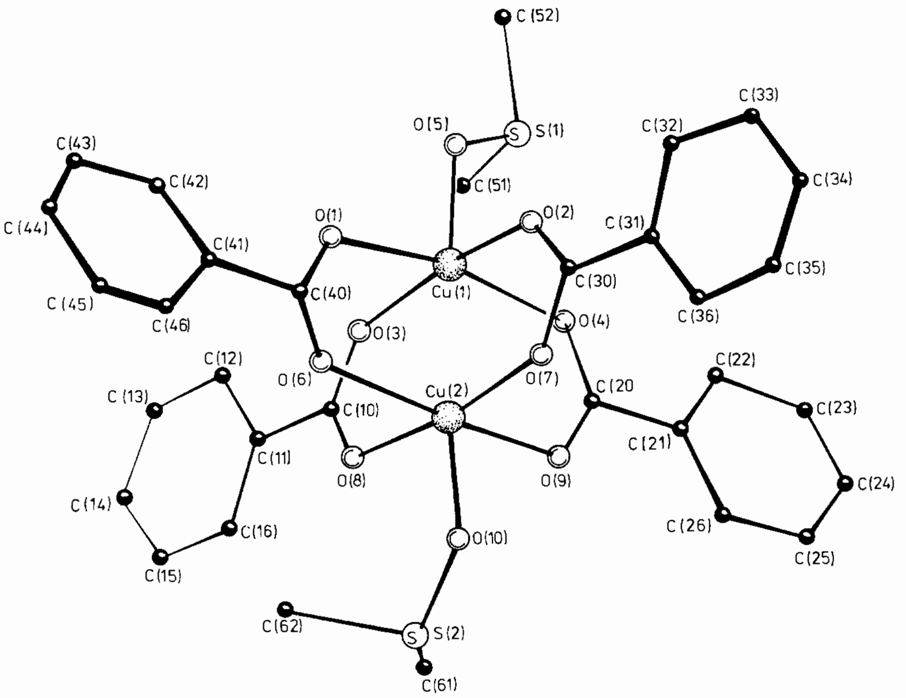

Fig. 1. A detailed view of the $[Cu(C_6H_5COO)_2DMSO]_2$ structure.

The DMSO molecule is coordinated through oxygen to the copper(II) atom. This coordination causes a slight shortening of the S–O bond in the DMSO group to 1.48(1) Å to that found in free DMSO [12], 1.531(8) Å and is consistent with a slight increase in $d \rightarrow p\pi$ bonding from sulfur to oxygen, caused by coordination [13]. The environment around the sulfur atom is distorted tetrahedral with the angle ranging from 97(1) to 107.1(9)°.

In Table IV are collected structural data for some copper(II) benzoates with the bridged binuclear structure. An attempt has been made to make this list complete as at the end of June 1982. We can see in Table IV that the axial ligand plays a role in determining the copper–copper distance. There exist some differences between the chromophore CuO_5 and CuO_4N, respectively. For instance, the sum of all interatomic distances in CuO_5 and CuO_4N (half the value of the Cu–Cu distances were also included in the sum of each chromophore) is approximately 11.33 and 11.42 Å, respectively. Also the Cu–O (basal) distances are somewhat longer in the CuO_4N chromophore (1.97 Å) than in the CuO_5 chromophore (1.96 Å). The values are the same as those reported [1] for copper(II) compounds containing binuclear units of this type. Some variation exists in the Cu–L (apical) distances, but this is not surprising.

The IR spectrum of $Cu(C_6H_5COO)_2DMSO$ shows the carboxylate stretching frequencies ν_{COO^-} (sym) at 1400 cm^{-1} and ν_{COO^-} (asym) at 1630 cm^{-1}. The positions of the bands are at a lower wave number than those found for the dimethylsulphoxide adduct of copper(II) benzoate studied by Bose and Patel

TABLE IV. Structural Data for Binuclear Copper(II) Benzoates.

Compound[a]	Cu–Cu (Å)	Cu–O (basal)[b] (Å)	Cu–L (apical) (Å)		O–C (Å)	Cu–O–C (degr)	O–C–O (degr)	Ref.
$Cu(C_6H_5COO)_2(dox)_{2.5}$	2.569(3)	1.963(8)	O[c]	2.178(9)	1.25(1)		124.7(8)	2
$Cu(C_6H_5COO)_2(CH_3OH)_2$	2.606(3)	1.95(2)	O	2.24(1)	1.26		125(2)	3
$Cu(C_6H_5COO)_2DMSO$	2.627(4)	1.963(15)	O	2.181(15)	1.262(27)	123.71(143)	123.96(204)	This work
$Cu(C_6H_5COO)_2quin$	2.671(2)	1.969(9)	N	2.186(8)				4
$Cu(C_6H_5COO)_2py$	2.681(1)	1.978(5)	N	2.184(7)	1.271(4)	122.8(5)	125.0(7)	5

[a] Dox, 1,4-dioxane; DMSO, dimethylsulfoxide; quin, quinoline; py, pyridine. [b] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. Estimated standard deviations in parentheses are average e.s.d.'s for an individual distance or angle. [c] The chemical identity of the apical atom is specified in this column.

[14]. In this connection, however, it should be noted that these latter workers did not specify which form of anhydrous copper(II) benzoate [15] was taken for the preparation of the adduct. The absorption band at about 1030 cm^{-1} has been attributed to the ν_{SO} stretching of coordinated DMSO. This band is shifted to a lower wave number compared with the corresponding band of the free DMSO [14] ($\nu_{SO} = 1055$ cm^{-1}).

The electronic spectrum of the title compound shows an absorption band at about 1.40 μm^{-1} and a shoulder at about 2.70 μm^{-1}; these values are different from those given by Bose and Patel [14] (1.527 and 2.86 μm^{-1}). It seems that 'disagreement' of the spectral results presented with the results quoted in [14] is caused by the fact that the sample measured by Bose and Patel and the title compound of the present work could be isomers.

The well-resolved EPR spectrum obtained for the polycrystalline title compound at room temperature shows absorption bands typical of the excited triplet state. The spin-Hamiltonian for triplet state binuclear copper(II) compounds is given by the equation

$$\mathcal{H} = g\beta HS + D(S_z^2 - 1/3S(S+1))$$

where S = 1 and D is the zero-field parameter, and other symbols have their usual meanings [16]. The observed values of $g_\perp = 2.07_1$, $g_\parallel = 2.35_4$ and $|D| = 0.346$ cm^{-1} are similar to those reported for binuclear copper(II) carboxylates [17].

The title compound has a subnormal magnetic moment at room temperature, suggesting that some coupling of the copper atoms occurs. The dependence of the magnetic susceptibility on temperature has been studied (Table V) and it has been found that it obeys the equation:

$$\chi_M^{exp} - N\alpha = \frac{g^2N\beta^2}{3kT}[1 + 1/3(\exp^{-2J/kT})]^{-1}$$

The symbols in the equation have their usual meanings. The spectroscopic splitting factor g_{av} was obtained from the EPR spectrum and was used as a constant in the least-squares fitting process. The criterion used for determination of the best fit was the minimization of the sum of the squares of the deviation A, where $A = \Sigma_i(\chi_i^{calc} - \chi_i^{exp})^2$; ($A = 4.25 \times 10^{-9}$). The value of $-2J = 304$ cm^{-1} is very close to that reported for binuclear copper(II) carboxylates [1].

Spectral and magnetic data for binuclear copper(II) benzoates are summarised in Table VI. Binuclear copper (II) benzoates tend to exhibit smaller values of g than copper(II) alkylcarboxylates [17, 29]. This may correlate [29] with the stronger ligand fields and the presence of a rhombic coordination sphere for the aryl compounds. In general, such a situation will lead to the mixture of the $|z^2>$ orbital with the ground state. For a such reason the value of g will be reduced [30].

TABLE V. Magnetic Data of $Cu(C_6H_5COO)_2DMSO$ ($-\Delta \cdot 10^6 = 186$).

T, K	$\chi_M^{corr} \cdot 10^6$	μ_{eff}, B.M.
82	129	0.29
102	230	0.43
111	287	0.505
122	387	0.61
133	422	0.67
143	483	0.74
153	544	0.82
164	613	0.89
175	660	0.96
185	702	1.02
195	725	1.06
206	736	1.10
216	759	1.145
226	786	1.19
239	798	1.235
251	817	1.28
262	825	1.315
272	831	1.345
282	825	1.365
296	825	1.40

It is evident (Table VI) that the value of $-2J$ for copper(II) benzoates rarely differ from its average (≈ 308 cm^{-1}) by more than 30 cm^{-1}. It is clear that the terminal ligands also influence these values. The $-2J$ value tends to increase according to the series of terminal ligands: nicotine < antipyrine < benzoic acid ~ aryl N-oxides < dimethylsulphoxide ~ butanol < pyridine < anhydrous ⩽ ethanol. Copper(II) alkylcarboxylates do not follow this trend [17, 29]. This observation indicates that the variation of $-2J$ with the terminal ligands is not a simple function of the base strength of the ligands.

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References

1 M. Melník, *Coord. Chem. Rev., 42*, 259 (1982).
2 L. Boniak, M. M. Borel, B. Fusnot and A. Leclaire, *Rev. Chim. Min., 16*, 501 (1979).
3 I. Bkouche-Waksman, C. Bois, G. A. Popovitch and P. L'Haridon, *Bul. Soc. Chim. France*, 69 (1980).
4 A. Bencini, D. Gatteschi and C. Mealli, *Cryst. Struct. Commun., 8*, 305 (1979).
5 B. T. Usubaliev, E. M. Movsumov, F. N. Musaev, G. N. Nadžafov, I. R. Amiraslanov and H. S. Mamedov, *Koord. Khim., 6*, 1091 (1980).

TABLE VI. Spectral and Magnetic Data for Binuclear Copper(II) Benzoates.

Compound ($X = C_6H_5COO^-$)	$g_\perp$	$g_\parallel$	g_{av}	$\lvert D \rvert$ (cm^{-1})	E (cm^{-1})	Electr. sp. (ν_{max} (μm^{-1})) I	II	$-2J$ (cm^{-1})	Ref.
CuX_2[a]			2.155	0.339	0.014	1.52	2.70	340[b]	18, 19
						1.50	2.05	312[c]	20
$CuX_2(CH_3OH)_2$	2.051(7)	2.342(7)	2.148(7)	0.330(5)	0.004(2)				21
$CuX_2C_2H_5OH$						1.445	2.70	340	15
$CuX_2C_2H_5OH \cdot H_2O$	2.067(7)	2.356(7)	2.163(7)	0.334(5)	0.003(2)				21
$CuX_2C_4H_9OH$						1.41	2.78	306	22
$CuX_2(CH_3COCH_3)_2$	2.064(7)	2.352(7)	2.160(7)	0.335(5)	0.003(2)				21
$CuX_2(CH_3COC_2H_5)_2$	2.061(7)	2.352(7)	2.158(7)	0.337(5)	0.003(2)				21
CuX_2dox	2.086	2.354	2.175	0.342		1.47	2.67		23
CuX_2dox$\cdot H_2O$	2.051(7)	2.342(7)	2.148	0.332(5)	0.003(2)				21
$CuX_2C_6H_5COOH$	[d]	2.345	2.147			1.48	2.70	310	15, 19
				0.341	0.006			288	18, 24
CuX_2DMF						1.534	2.86		14
CuX_2DMSO	2.071	2.354	2.165	0.346	0.003	1.40	2.70	304	This work
						1.527	2.86		14
CuX_2apy						1.34	2.65	≈285	25
CuX_2arNO[e]						≈1.36	≈2.67	≈298	26
CuX_2py						1.375	2.70	310	15
CuX_2quin	2.07	2.32	2.153						27
CuX_2nic	2.092	2.354	2.179	0.362		1.35	2.60	253	28
CuX_2an	[f]	2.357	2.16	0.3436	0.0374			320	31
$CuX_2(4,4'\text{-bipy})_{0.5}$						1.355	2.70	300	15
CuX_2qox	2.06	2.32	2.14	0.34					27

Abbreviations: dox, 1,4-dioxane; DMF, dimethylformamide; DMSO, dimethylsulfoxide; apy, antipyridine; arNO, aryl-N-oxide; py, pyridine; quin, quinoline; nic, nicotine; an, aniline; 4,4'-bipy, 4,4'-bipyridyl; qox, quinoxaline.

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[a] EPR at 77 K, $g_x = 2.048(4)$; $g_y = 2.074(4)$; $g_z = 2.345(4)$; $D = 0.3311(6)$ cm^{-1}; $E = 0.0147(3)$ cm^{-1}. [b] Methanol adduct of copper(II) benzoate was heated in vacuum at the temperature of boiling CCl_4 for 3 hours. [c] Trihydrate copper(II) benzoate was refluxed in acetone for several hours. [d] $g_x = 2.048$; $g_y = 2.074$. [e] aryl-NO, pyridine N-oxide; 2-picoline N-oxide; 3-picoline N-oxide; 4-picoline N-oxide; 2,6-lutidine N-oxide; 2,4,6-collidine N-oxide; quinoline N-oxide; quinaldine N-oxide; lepidine N-oxide. [f] $g_x = 2.056$; $g_y = 2.062$.

6 F. Ephraim and A. Pfister, *Helv. Chim. Acta, 8*, 374 (1925).

7 M. Melník and J. Moroziński, *J. Mol. Struct., 78*, 85 (1982).

8 'International Tables for X-Ray Crystallography', Vol. 1, Kynoch Press, Birmingham 1952.

9 'XTL/E-XTL Structure Determination Systems Operation Manuel', Syntex Analytical Instruments, Inc. Cuperlino, 1976.

10 F. R. Ahmed, 'Crystallographic Computing', Munksgaard, Copenhagen, 1970, p. 55.

11 D. T. Cromer and J. Waber, *Acta Cryst., 18*, 104 (1965).

12 R. Thomas, C. B. Shoemaker and K. Eriks, *Acta Cryst., 21*, 12 (1966).

13 M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams and W. H. Watson, *ibid., 23*, 788 (1967).

14 K. S. Bose and C. C. Patel, *Indian J. Chem., 8*, 840 (1970).

15 J. Lewis and F. Mabbs, *J. Chem. Soc.*, 3894 (1965).

16 B. Bleaney and K. D. Bowers, *Proc. R. Soc., Ser. A, 214*, 451 (1952).

17 M. Melník, *Coord. Chem. Rev., 36*, 1 (1981) and refs. therein.

18 Yu. V. Jablokov, V. V. Zelentsov and L. N. Romanenko, *Teor. Experim. Khim., 4*, 407 (1968).

19 F. G. Herring, R. C. Thompson and C. F. Schwerdtfeger, *Can. J. Chem., 47*, 555 (1969).

20 J. Lewis, Y. C. Lin, L. K. Royston and R. C. Thompson, *J. Chem. Soc.*, 6464 (1965).

21 G. A. Popovitch, A. V. Ablov, Yu. V. Jablokov and G. A. Kiosse, *Zh. Neorg. Khim., 16*, 591 (1971).

22 W. E. Hatfield, C. S. Fountain and R. Whyman, *Inorg. Chem., 5*, 1855 (1966).

23 M. Melník and R. Uggla, *Suom. Kemistilehti B, 43*, 499 (1970).

24 V. V. Zelentsov, M. N. Volkov, V. M. Allenov and T. G. Aminov, *Zh. Neorg. Khim., 10*, 564 (1965).

25 J. K. Šmogrovič, J. Kohout and K. Staiger, *Z. Chem., 11*, 26 (1971).

26 M. Melník and J. K. Šmogrovič, *Chem. zvesti, 27*, 594 (1973).

27 F. G. Herring, F. E. Mabbs, L. K. Royston and W. R. Smail, *J. Chem. Soc. A*, 291 (1969).

28 M. Melník, *J. Inorg. Nucl. Chem., 41*, 779 (1979).

29 R. W. Jotham, F. A. Kettle and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, 428 (1972).

30 R. N. Bagchi and P. Sengupta, *Indian J. Phys., 40*, 675 (1966).

31 F. G. Herring, B. Landl, R. C. Thompson and C. F. Schwerdtfeger, *J. Chem. Soc. A*, 528 (1971).