Crystal Structure and Magnetic Properties of the β-Modification of Diaquatetrakis(μ-2-methoxybenzoato-*O,O'*)dicopper(II)

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The crystal structure of the β-modification of $Cu_2(o\text{-}CH_3OC_6H_4COO)_4 \cdot 2H_2O$ has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in space group $P2_1/c$ with the unit-cell dimensions: $a = 20.6566(12)$, $b = 7.2799(10)$, $c = 21.3486(25)$ Å, $\beta = 93.890(6)°$. The structure was solved with heavy-atom methods which gave the positions of the copper atoms. All the other non-hydrogen atoms were located by successive Fourier and difference Fourier syntheses. The structure was refined with least-squares calculations to a conventional R-value of 0.057 for 1226 unique reflections with $F/\sigma(F) \geq 6$.

The asymmetric unit consists of a dimeric Cu-complex of the copper(II) acetate type. In accordance with the carboxylate-bridged dinuclear structure, the cryomagnetic behaviour of the studied compound (temperature range 90–330 K) is typical of a spin–spin coupled Cu(II)-complex with a singlet ground state separated by $2J = -284$ cm^{-1} from the triplet excited state.

By reaction of Cu^{2+} and o-MOB^- ions (o-MOB = 2-methoxybenzoate) in aqueous solution, two differently coloured samples of the composition $Cu(o\text{-}MOB)_2 \cdot H_2O$ resulted, depending on the concentration of the reaction mixtures.[1] The two samples presented completely different X-ray powder diffraction patterns. The blue–green modification, precipitated from more concentrated solutions, was named α; the green-coloured compound obtained by slow crystallization from dilute solutions was denoted β. The magnetic and spectral properties of the α- and β-modifications of $Cu(o\text{-}MOB)_2 \cdot 2H_2O$ indicate that the presence of antiferromagnetically coupled dinuclear complex molecules $Cu_2(o\text{-}MOB)_4 \cdot 2H_2O$ is the fundamental structural motif in both forms.[2]

In the present paper we report the structural and magnetic properties of the β-modification, which could be prepared as sufficiently well developed single crystals.

The structures and properties of the 2-methoxybenzoatocopper(II) complexes also have interesting bioinorganic and pharmaceutical aspects because of the antiphlogistic and antipyretic activities of the compounds.[3]

Experimental

The dark green β-modification of $Cu_2(o\text{-}MOB)_4 \cdot 2H_2O$ was prepared by mixing solutions of 2.90 g of o-$CH_3OC_6H_4COONa$ in 240 ml of water and 2.05 g of $CuSO_4 \cdot 5H_2O$ in 60 ml of water at room temperature.[1] Chemical analysis corroborated the formula. A crystal of approximate dimensions 0.05×0.05×0.15 mm was selected for X-ray analysis. Intensities were collected at room temperature on a Siemens STOE/AED2 diffractometer, equipped with a graphite monochromator to reflect Mo$K\alpha$ radiation. Systematic absences $h0l : l = 2n+1$ and $0k0 : k = 2n+1$ indicated space group $P2_1/c$.

Lattice parameters were determined by least-squares refinement based on 2θ-values of 42 selected reflections. Crystal data are given in Table 1. Intensities were mea-

Table 1. Crystal data.

Space group	$P2_1/c$
a/Å	20.6566(12)
b/Å	7.2799(10)
c/Å	21.3486(25)
β/°	93.890(6)
V/Å^3	3202.9(6)
Z	4
$F(000)$	1576
2θ range/°	2–50
Measured reflections	4344
Unique observed reflections	1256
μ(Mo$K\alpha$)/cm^{-1}	13.65
Final R ($\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$)	0.057
Final R_w ($\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2)^{1/2}$	0.049

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sured between 2.0 and 50.0° by the ω-2θ scan mode at a speed of 0.02° s^{-1} and a scan width of 1.0°.

The background was measured at each end of the scan interval. Ten reflections were monitored periodically once every 100 min during the data collection and showed no sign of crystal deterioration. The data were corrected for Lorentz, polarization and absorption effects (μ = 13.65 cm^{-1}).

Calculations were carried out with the program SHELX-76.[4] The figures were drawn with the PLUTO program.[5] Scattering factors and corrections for anomalous dispersion were taken from Ref. 6. The magnetic susceptibility of powdered samples of the studied complex was determined by the Gouy method on an apparatus equipped with a liquid-nitrogen cryostat (Newport Instruments Ltd.). The temperature range was 90–330 K, and four different values of the magnetic induction, in the range 0.4–0.7 T, were used. $Hg(Co(SCN)_4)$ was used as a standard.[7] The molar susceptibility was corrected for the diamagnetism of the components, using the appropriate Pascal constants,[8] $\Sigma\chi_{dia} = -249\times10^{-11}$ m^3 mol^{-1}, and for the TIP (temperature-independent paramagnetic contribution) of copper, $TIP_{Cu} = 75\times10^{-11}$ m^3 mol^{-1}.[9] The parameters of these magnetic properties are summarized in Table 2.

Structure determination and refinement

The structure was solved by a combination of Patterson function and Fourier methods. The two copper atoms were determined from a Patterson map, and all the other non-hydrogen atoms by successive Fourier and difference Fourier calculations. A total of 4344 reflections were measured. After merging, 1256 unique reflections had $F/\sigma(F) \geq 6$ and were considered observed. The four aromatic rings were treated as rigid groups. The positions of the hydrogens on the aromatic rings were calculated from geometric considerations, and were given the same temperature factors as the carbons to which they were connected. Both copper atoms and all ten oxygens nearest to them were refined anisotropically, all other atoms isotropically. In the final cycles of refinement the weighting scheme $w = 2.1952/[\sigma^2(F)]$ was employed. There were no changes larger than 0.01σ in any of the positional parameters varied in the final refinement cycle. The total number of parameters was 205. The final conventional R-factor was 0.057 and the weighted R-factor was 0.049. Atomic coordinates

Table 2. Cryomagnetic properties of $Cu_2(o\text{-MOB})_4\cdot 2H_2O$.

T/K	$10^{11}\ \chi_M$/m^3 mol^{-1}	μ_{eff}/B.M.
338	1185	1.54
330	1221	1.55
308	1201	1.49
301	1247	1.50
279	1234	1.43
272	1259	1.43
251	1235	1.36
241	1243	1.34
220	1200	1.25
210	1188	1.22
192	1121	1.13
182	1064	1.07
162	964	0.96
131	809	0.78
121	722	0.71
112	609	0.62
102	493	0.52
92	390	0.43

Table 3. Atomic coordinates, estimated standard deviations and U_{eq} ($U_{eq} = \frac{1}{3}\Sigma\Sigma a_i a_j a_i^* a_j^*$).

Atom	x	y	z	U_{eq}
Cu1	0.2383(2)	1.1954(3)	0.2279(1)	0.019(2)
Cu2	0.2663(2)	0.8788(3)	0.2807(2)	0.022(2)
O1	0.2236(7)	1.4603(17)	0.1852(7)	0.022(6)
O2	0.2809(7)	0.6072(18)	0.3229(7)	0.025(6)
O3	0.2989(8)	0.8122(22)	0.1981(8)	0.043(8)
O4	0.2795(7)	1.0883(20)	0.1570(7)	0.027(6)
O5	0.1583(7)	1.0709(20)	0.1969(8)	0.035(7)
O6	0.1785(7)	0.7973(19)	0.2420(7)	0.026(6)
O7	0.3220(7)	1.2684(21)	0.2689(7)	0.034(7)
O8	0.3485(7)	0.9978(21)	0.3092(7)	0.026(7)
O9	0.2013(7)	1.2600(20)	0.3065(7)	0.026(7)
O10	0.2274(8)	0.9915(22)	0.3521(8)	0.036(7)
C1	0.2984(11)	0.9213(38)	0.1540(12)	0.024(7)
C2	0.3503(7)	0.6250(14)	0.0189(7)	0.043(7)
C3	0.3401(7)	0.7477(14)	−0.0310(7)	0.044(7)
C4	0.3176(7)	0.9248(14)	−0.0202(7)	0.030(7)
C5	0.3053(7)	0.9793(14)	0.0405(7)	0.041(8)
C6	0.3154(7)	0.8565(14)	0.0904(7)	0.018(6)
C7	0.3380(7)	0.6794(14)	0.0796(7)	0.029(7)
O11	0.3487(8)	0.5618(21)	0.1283(8)	0.055(6)
C8	0.3879(13)	0.3958(32)	0.1199(13)	0.044(8)
C9	0.1451(12)	0.9025(40)	0.2083(12)	0.030(8)
C10	−0.0230(5)	0.7318(18)	0.1515(6)	0.035(6)
C11	−0.0109(5)	0.6640(18)	0.0923(6)	0.041(7)
C12	0.0514(5)	0.6751(18)	0.0711(6)	0.046(7)
C13	0.1015(5)	0.7539(18)	0.1090(6)	0.034(6)
C14	0.0894(5)	0.8217(18)	0.1681(6)	0.025(6)
C15	0.0272(5)	0.8106(18)	0.1894(6)	0.026(5)
O12	0.0199(6)	0.8747(20)	0.2490(6)	0.034(4)
C16	−0.0423(12)	0.8515(31)	0.2771(11)	0.044(8)
C17	0.2055(10)	1.1561(33)	0.3533(10)	0.019(6)
C18	0.1371(7)	1.4333(15)	0.4848(7)	0.033(7)
C19	0.1475(7)	1.3113(15)	0.5348(7)	0.043(7)
C20	0.1780(7)	1.1432(15)	0.5258(7)	0.043(7)
C21	0.1981(7)	1.0971(15)	0.4668(7)	0.036(7)
C22	0.1877(7)	1.2191(15)	0.4168(7)	0.028(7)
C23	0.1572(7)	1.3872(15)	0.4257(7)	0.032(7)
O13	0.1488(8)	1.5090(20)	0.3770(8)	0.044(5)
C24	0.1085(14)	1.6738(32)	0.3806(14)	0.055(9)
C25	0.3568(11)	1.1664(31)	0.3041(10)	0.020(7)
C26	0.4905(6)	1.4928(15)	0.3723(6)	0.039(7)
C27	0.5104(6)	1.3961(15)	0.4266(6)	0.051(7)
C28	0.4820(6)	1.2277(15)	0.4393(6)	0.052(7)
C29	0.4336(6)	1.1560(15)	0.3976(6)	0.040(7)
C30	0.4137(6)	1.2527(15)	0.3433(6)	0.019(6)
C31	0.4421(6)	1.4211(15)	0.3306(6)	0.030(6)
O14	0.4223(7)	1.5048(20)	0.2751(7)	0.047(5)
C32	0.4547(11)	1.6747(32)	0.2576(12)	0.045(7)

and thermal parameters are listed in Table 3. A list of observed and calculated structure factors can be obtained on request from one of the authors (P.-E. W.).

Description of the structure

The asymmetric unit consists of one dinuclear complex (Fig. 1) in which the copper atoms are bridged in pairs by four carboxylate groups. Each copper atom is joined to four oxygens lying in a plane which is approximately normal to the intramolecular Cu–Cu vector. The average length of the 8 Cu–O bonds is 1.966 (0.019) Å (Table 4). The average value of the Cu–O(water) distance is 2.173 Å (Table 4), thus giving the copper atoms a slightly distorted square-pyramidal coordination, similar to the geometry of the copper(II) acetate monohydrate complex.[10] A stereoscopic figure showing the packing in the unit cell is shown in Fig. 2. Among the dinuclear carboxylatocopper(II) complexes the existence of modifications with small differences in the molecular structure but relevant differences in the crystal structure is known. For example, dipyridinetetrakis-(μ-acetato-*O,O'*)dicopper(II) occurs in monoclinic[11] and orthorombic[12] modifications, with Cu–Cu distances of 2.630(3) and 2.70 Å, respectively. Furthermore, the EPR spectrum of the α-modification of $Cu_2(o\text{-MOB})_4 \cdot 2H_2O$ can be interpreted by assuming an overlapping of two closely adjacent lines connected with the transition in two types of similar dimeric Cu(II)-complex molecules, α_1 and α_2.[2] The EPR spectrum of the β-modification, however, does not reveal any corresponding split.[2]

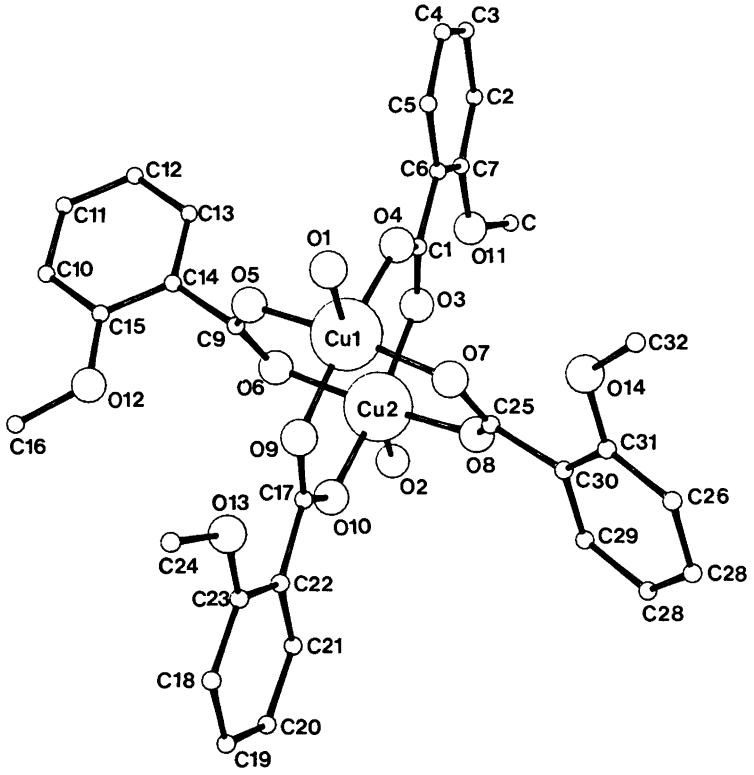

Fig. 1. Numbering scheme of the complex.

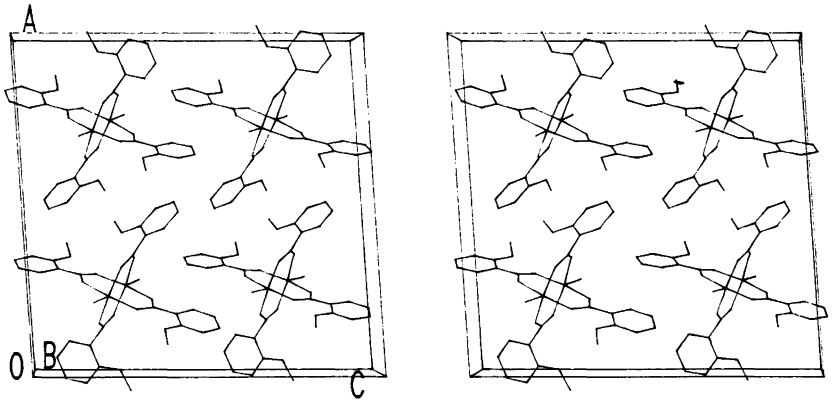

Fig. 2. Stereoscopic view of the structure showing the unit cell and the packing arrangement.

Table 4. Interatomic distances (Å) with estimated standard deviations.

Atoms	Distance	Atoms	Distance
Cu1–O9	1.949(15)	Cu2–O10	1.952(17)
Cu1–O4	1.950(15)	Cu2–O8	1.966(15)
Cu1–O7	1.958(15)	Cu2–O3	1.990(17)
Cu1–O5	1.960(15)	Cu2–O6	2.030(15)
Cu1–O1	2.146(13)	Cu2–O2	2.186(14)
Cu2–Cu2	2.614(4)	Cu2–Cu1	2.614(4)

Magnetic properties of the complex

The temperature dependence of the magnetic susceptibility of the studied complex was evaluated by the Bleany–Bowers equation for $s = 1/2$ coupled dimers,[13] used in the form of eqn. (1).

$$\chi_M = (1-x)\frac{Ng_D^2\beta^2}{kT}\left[3+\exp\left(\frac{-2J}{kT}\right)\right]^{-1} + x\frac{Ng_M^2\beta^2}{4kT} + \text{TIP} \quad (1)$$

The electron splitting factor for the dimer is denoted g_D, and for the mononuclear impurity, g_M. The value of the latter determined from the EPR spectrum is $g_M = 2.165$. The molar fraction of the mononuclear impurity is denoted x. The other symbols have their usual meanings. The observed magnetic susceptibility data (18 values) were fitted to eqn. (1). In the fitting procedure all experimentally observed susceptibilities were weighted, and the best values of g_D, $2J$ and x were taken to be those which minimized eqn. (2).

$$D = \Sigma[(\chi'_{M,exp} - \chi'_{M,calc})/\chi'_{M,exp}]^2 \quad (2)$$

The temperature dependence of χ'_M corrected for diamagnetism is illustrated in Fig. 3. The cryomagnetic behaviour of the studied complex is typically antiferromagnetic. It displays a subnormal room-temperature magnetic moment $\mu_{eff} = 1.43$ B.M. and a magnetic susceptibility maximum (T_n) at $T \approx 270$ K. Both these parameters μ_{eff} and χ'_M fall steeply with decreasing temperature below T_n. The best fit ($D = 1.83\times10^{-2}$) of eqn. (1) to the observed χ'_M vs. T data was obtained for $2J = -284$ cm^{-1} (5.64×10^{-21} J), $g_D = 2.25$ and $x = 0.2$ % (mononuclear impurity), by using the normal value of $\text{TIP}_{Cu} = 75\times10^{-11}$ m^3 mol^{-1}. The Neel temperature, $T_n = 255$ K, was calculated from $2J = 8/5\ kT_n$, using the best-fit value of the singlet–triplet separation, $2J = -284$ cm^{-1}. If the TIP is allowed to vary in the fitting procedure a more realistic value of g_D can be obtained, but the TIP is higher in this case: $2J = -293$ cm^{-1}, $g_D = 2.21$, $\text{TIP}_{Cu} = 134\times10^{-11}$ m^{3}mol^{-1} and $x = 0.2$ %, with $D = 1.21$

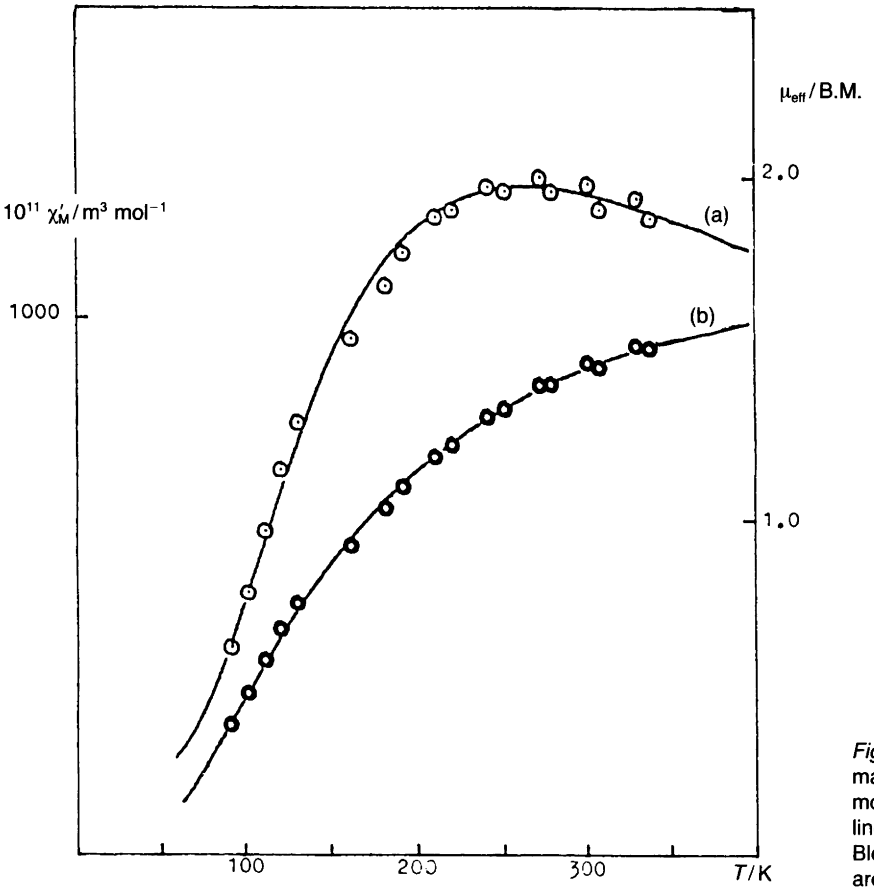

Fig. 3. Temperature dependence of the magnetic susceptibility (a) and the magnetic moment (b) of $[Cu_2(o\text{-MOB})_4 \cdot 2H_2O]$. The full lines represent the calculated values of the Bleany–Nowers equation. Experimental points are indicated by circles.

$\times 10^{-2}$. The magnetic behaviour of $Cu_2(o\text{-MOB})_4 \cdot 2H_2O$ is in very good agreement with the dinuclear carboxylate-bridged structure, in which Cu(II) ions of spin 1/2 interact within isolated pairs to form a singlet, $S = 0$, ground state and an excited triplet state, $S = 1$. The similarity of the structure of the studied complex to that of diaquatetrakis-(μ-acetato-*O,O'*)dicopper(II),[10,14,15] is expressed in the closely related magnetic properties of these compounds, including their identical values of the singlet–triplet separation.

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