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The Crystal and Molecular Structure of Diaquatetrakis(μ-2-nitrophenoxyacetato-*O*,*O'*)dicopper(II) Dihydrate

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The crystal structure of diaquatetrakis-(μ-2-nitrophenoxyacetato-*O*,*O'*)dicopper(II) dihydrate, $[(NO_2C_6H_4OCH_2COO)_2Cu(H_2O)]_2 \cdot 2H_2O$, has been determined by single crystal X-ray diffraction methods. The structure has been determined and refined in the triclinic space group $P\bar{1}$ with the unit cell dimensions a=16.175(5), b=8.081(2), c=7.710(2)Å, α=103.48(4), β=96.58(3), γ=94.81(4)°.

Intensity data were collected on a diffractometer with Mo$K\alpha$ radiation. The final R index for 2409 reflections is 0.071. The structure consists of a dinuclear complex, in which two copper atoms are bridged in pairs by four carboxylate-groups, and with two water molecules occupying terminal positions. The copper-copper distance is 2.655(2) Å. The dimeric structure proposed on the basis of magnetic properties has been confirmed by the results of the crystal structure determination.

The copper(II)aryloxyacetates exhibit interesting properties from the point of view of the carboxylatocopper(II) complexes of various structures. At least three different forms of the phenoxyacetatocopper (II) complexes may be obtained from the reaction mixtures in aqueous solution containing Cu^{2+} and $C_6H_5OCH_2COO^-$ ions. The anhydrous copper(II)phenoxyacetate forms hexameric complex molecules, in which the carboxylate groups form both syn-syn and syn-anti bridges.[1] The diaquabis(phenoxyacetato)copper(II) is a distorted octahedral *trans*-complex[2] with bidentate phenoxyacetate ligands forming long Cu–O (phenoxy) and short Cu–O (carboxylate) contacts. The triaquabis(phenoxyacetato)-copper(II) represents a square pyramidal complex with unidentate phenoxyacetates.[3] On the other hand, Hatfield *et al.*,[4] have prepared the copper(II)-phenoxyacetate monohydrate from dilute ethanol solutions, which exhibits a room temperature magnetic moment (μ_{eff} 300 K=2.00 B.M.), in excess of the spin value 1.73 B.M..

Sometimes, the structure and properties of the aryloxyacetatocopper(II) complexes are affected by the influence of the substituents on the phenyl ring. The moderate room temperature magnetic moment (μ_{eff}=1.57 B.M.) for the copper(II)-p-nitrophenoxyacetate

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trihydrate border on the range ascribed to polymeric materials,[4] whereas the room temperature magnetic moment (μ_{eff}=1.35 B.M.) for the copper(II)-o-nitrophenoxyacetate dihydrate[5] suggests a binuclear structure. This is in good agreement with the fact that the presence of bulky ortho-substituents in the arylcarboxylate series favours the formation of binuclear complexes over more polymeric structures, irrespective of other factors.

Prout *et al.*[6] have prepared the mononuclear diaquabis(*p*-nitrophenoxyacetato)copper-(II) complex, and its crystal data were reported. The magnetic moment at room temperature for this compound (μ_{eff}=1.87 B.M.) is typical of the magnetically diluted Cu(II) complexes with tetragonal symmetry.[7]

It must be pointed out that the difference in hydration of the different substituted compounds may indicate a major difference in structural features. The present investigation was undertaken in order to determine the nature of the Cu coordination in the title compound.

EXPERIMENTAL

Diaquatetrakis(μ-2-nitrophenoxyacetato-O,O′)dicopper(II) dihydrate $[(NO_2C_6H_4OCH_2COO)_2Cu(H_2O)]_2 \cdot 2H_2O$ was prepared by the following procedure:

2-nitrophenoxyacetic acid (0.5 mol) and $NaHCO_3$ (0.5 mol) were dissolved in 1700 ml of hot water. The reaction mixture was heated to remove CO_2. After that, the pH of the solution was adjusted to 4.5–5.0 by 2-nitrophenoxyacetic acid, then 300 ml of hot H_2O solution of $CuSO_4 \cdot 5H_2O$ (0.25 mol) was added. A green crystal product was obtained by cooling the solution. The crystals were stable in air and were of a size suitable for X-ray work.

The product was analysed for copper, carbon, nitrogen and hydrogen. The results were Cu 12.9 %, C 38.9 %, N 5.8 % and H 3.3 %, which are in good agreement with the calculated values (Cu 12.92 %, C 39.07 %, N 5.69 % and H 3.28 %) for the formula $C_{16}H_{12}N_2O_{10}Cu(H_2O)_2$.

A crystal of approximate dimensions 0.3×0.2×0.25 mm^3 was selected for X-ray analysis. The unit cell parameters and the rotation matrix were determined by a least-squares refinement from 25 centered reflections measured at ambient temperature on a Philips PW1100 diffractometer. Intensity data were collected ($5° < 2\theta < 60°$) in the θ-2θ scan mode, using graphite-monochromatized Mo$K\alpha$ radiation. The scan width was 1.8° and the scan speed 1.8° min^{-1} in θ. The background was measured at each end of the interval for half the scan time. Three selected reflections were monitored as standards after every 44 measurements. Their intensities showed no significant changes with time. The intensities were corrected for Lorentz and polarisation effects but not for absorption (μ=12 cm^{-1}). Out of 5582 reflections, 2409 were refined in the subsequent least-squares calculations, using an acceptance criterion $|F_o| > 5\sigma(F_o)$. Crystal data are given in Table 1. The final atomic coordinates and their estimated standard deviations are summarized in Table 2.

Calculations were carried out with the SHELX program system.[8] The figures were drawn with the PLUTO 78 program.[9] The atomic scattering factors used were those of Cromer and Waber.[10]

Table 1. Crystal data.

$[(NO_2C_6H_4OCH_2COO)_2Cu(H_2O)]_2\ 2H_2O$
F.W.=983.69
Space group: $P\bar{1}$ (No. 2)
a=16.175(5), b=8.081(2), c=7.710(2) Å;
α=103.48(4), β=96.58(3), γ=94.81(4)°;
V=967.2 Å^3, Z=1, F(000)=498;
μ(Mo$K\alpha$)=12 cm^{-1}, λ(Mo$K\alpha$)=0.71069 Å; D_x=1.69 g cm^{-3}

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$), with e.s.d.'s in parentheses.

	x	y	z	U_{eq}[a]
Cu	10287(1)	1356(1)	4458(1)	20(1)
C1	7282(5)	−3546(10)	−1299(11)	31(3)
C2	7484(5)	−3394(11)	−2946(11)	32(3)
C3	6965(6)	−4241(12)	−4504(12)	46(4)
C4	6234(6)	−5245(12)	−4453(13)	49(4)
C5	5999(6)	−5390(12)	−2824(13)	45(4)
C6	6521(5)	−4503(11)	−1249(11)	35(3)
C7	8497(5)	−1740(11)	265(11)	36(3)
C8	8997(5)	−1082(10)	2136(11)	28(3)
N1	6226(6)	−4566(11)	462(11)	53(4)
O1	6219(7)	−3202(13)	1563(12)	103(5)
O2	5912(9)	−5821(14)	700(14)	139(7)
O3	7772(4)	−2805(8)	336(7)	44(3)
O4	9446(4)	298(7)	2357(7)	34(2)
O5	8936(4)	−1970(7)	3281(7)	35(2)
C11	7179(5)	1067(10)	8129(11)	31(2)
C12	6897(6)	551(11)	6273(12)	38(3)
C13	6148(6)	−455(13)	5631(13)	48(4)
C14	5629(6)	−939(13)	6785(15)	53(4)
C15	5895(5)	−448(12)	8604(13)	42(4)
C16	6645(5)	560(11)	9265(11)	32(3)
C17	8381(6)	2804(11)	7674(13)	40(4)
C18	8948(4)	1618(10)	6656(10)	25(3)
N11	6854(6)	1077(11)	11243(11)	50(4)
O11	7578(5)	1551(12)	11932(10)	78(4)
O12	6282(5)	1005(13)	12133(10)	84(4)
O13	7915(3)	2953(8)	8838(7)	36(2)
O15	9409(3)	2374(6)	5812(7)	30(2)
O14	8908(3)	85(7)	6710(7)	32(2)
OW1	10510(4)	3673(7)	3507(8)	37(2)
OW2	11071(6)	−4408(9)	7585(13)	99(4)

[a] U_{eq} is calculated from the refined anisotropic thermal parameters.

$$U_{eq} = \tfrac{1}{3} \cdot \sum_i \cdot \sum_j \cdot U_{ij} \cdot a_i \cdot a_j \cdot \bar{a}_i \cdot \bar{a}_j$$

STRUCTURE DETERMINATION

The structure was solved by conventional methods. A possible copper position was derived from the Patterson function, and subsequent Fourier syntheses carried out in space group $P\bar{1}$ revealed the positions of all C, N and O atoms. The choice of $P\bar{1}$ as the correct space group was justified by the successful refinement of the structure. The structure was refined by the full-matrix least-squares method, first isotropically, then with anisotropic temperature factors for all nonhydrogen atoms. Hydrogen atoms, except those bound to the water molecules, were included at calculated positions. The final R-value was 0.071 and the weighted discrepancy factor R_w was 0.069. The weighting scheme was $w^{-1} = \sigma^2(F_o) + 0.0019|F_o|^2$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

A list of observed and calculated structure factors can be obtained on request from the Department of Structural Chemistry, University of Stockholm, S-106 91 Stockholm, Sweden.

Table 3. Bond lengths (Å) and selected bond angles (°) with e.s.d.'s in parentheses.

a. Copper coordination. The symmetry operation used to generate the positions of the primed atoms is: $2-x,-y,1-z$			
Cu–Cu′	2.655(2)	O4–Cu–O14′	88.1(2)
Cu–O4	1.966(5)	O4–Cu–O15	90.8(2)
Cu–O5′	1.965(5)	O5′–Cu–O14′	88.5(2)
Cu–O14′	1.974(5)	O5′–Cu–O15	88.6(2)
Cu–O15	1.979(5)	O4–Cu–Ow1	92.0(2)
Cu–Ow1	2.181(5)	O5′–Cu–Ow1	100.1(2)
		O14′–Cu–Ow1	101.8(2)
		O15–Cu–Ow1	90.2(2)
b. Ligand bond lengths			
C1–C2	1.376(11)	C11–C12	1.404(12)
C1–C6	1.407(11)	C11–C16	1.401(11)
C1–O3	1.386(9)	C11–O13	1.357(10)
C2–C3	1.381(11)	C12–C13	1.373(13)
C3–C4	1.387(13)	C13–C14	1.388(14)
C4–C5	1.380(13)	C14–C15	1.373(13)
C5–C6	1.401(11)	C15–C16	1.376(12)
N1–C6	1.463(12)	N11–C16	1.476(11)
N1–O1	1.227(11)	N11–O11	1.220(10)
N1–O2	1.158(11)	N11–O12	1.218(10)
C7–C8	1.525(11)	C17–C18	1.529(10)
C7–O3	1.409(10)	C17–O13	1.439(10)
C8–O4	1.244(9)	C18–O14	1.246(9)
C8–O5	1.268(9)	C18–O15	1.254(8)
c. Ligand bond angles			
C2–C1–C6	118.4(8)	C12–C11–C16	116.6(8)
C2–C1–O3	124.7(8)	C12–C11–C13	123.3(7)
C6–C1–O3	116.9(7)	C16–C11–O13	120.1(7)
C1–C2–C3	120.0(8)	C11–C12–C13	120.7(8)
C2–C3–C4	121.4(9)	C12–C13–C14	121.5(9)
C3–C4–C5	120.3(8)	C13–C14–C15	118.4(9)
C4–C5–C6	118.0(8)	C14–C15–C16	120.6(9)
C1–C6–C5	121.8(8)	C11–C16–C15	122.0(8)
C1–C6–N1	121.2(7)	C11–C16–N11	121.9(8)
C5–C6–N1	117.0(8)	C15–C16–N11	116.2(8)
C6–N1–O1	117.6(9)	C16–N11–O11	120.1(8)
C6–N1–O2	121.7(9)	C16–N11–O12	117.6(9)
O1–N1–O2	120.0(10)	O11–N11–O12	122.3(9)
C1–O3–C7	115.9(6)	C11–O13–C17	118.9(7)
O3–C7–C8	110.3(7)	O13–C17–C18	114.1(7)
C7–C8–O4	114.5(7)	C17–C18–O14	120.3(7)
C7–C8–O5	118.9(7)	C17–C18–O15	112.1(7)
O4–C8–O5	126.6(7)	O14–C18–O15	127.6(7)

RESULTS AND DISCUSSION

Intramolecular bond distances and selected bond angles are listed, with their estimated standard deviations, in Table 3. The numbering scheme of the centrosymmetrical complex is shown in Fig. 1 and a stereoscopic view of the compound, including crystal water, is given in Fig. 2.

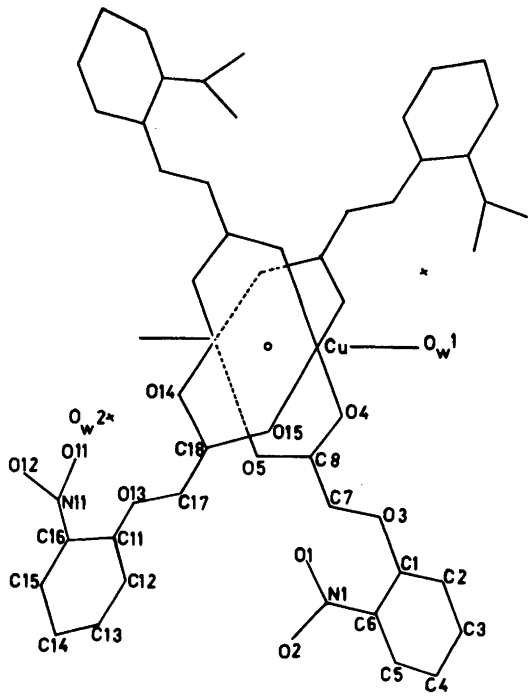

Fig. 1. Numbering scheme of the molecule.

The structure consists of a dinuclear molecule, in which two copper atoms are bridged in pairs by four carboxylate groups, and with two water molecules occupying terminal positions (Fig. 2). The copper(II) ion is 0.21 Å out of the plane of four oxygen atoms from the carboxylate groups. The copper coordination is almost identical with that found for copper(II)acetate monohydrate.[11] The copper-copper distance in the present compound is 2.655(2)Å, and the elongated copper-oxygen bond to the coordinated water is 2.181(5) Å.

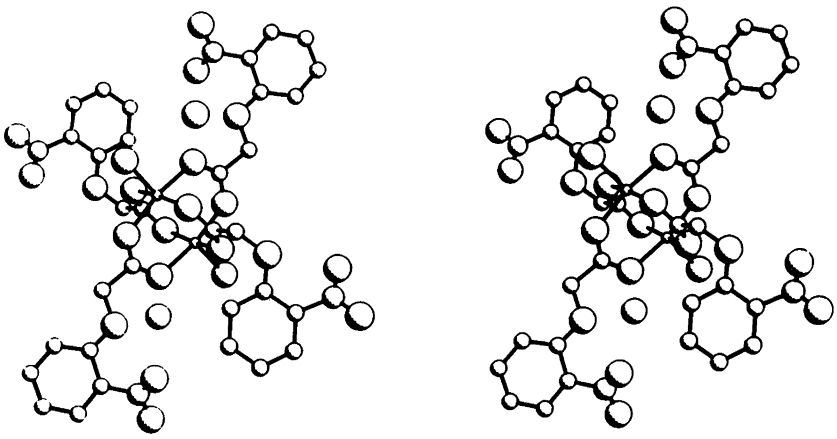

Fig. 2. Stereoscopic view of the molecule.

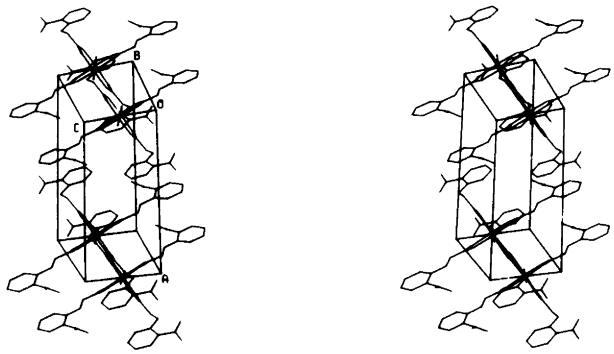

Fig. 3. A perspective view of the structure, showing the unit-cell and the packing arrangement.

The corresponding distances for copper(II)acetate monohydrate are 2.6143(17) and 2.1613(17) Å, respectively,[11] and the Cu–Cu distances in tetra-μ-acetatobisaquadicopper-(II) is 2.616 Å.[12] It is notable, however, that if the nitro-group in the present diaquatetrakis(μ-2-nitrophenoxy-acetato-*O,O'*)dicopper(II) dihydrate is moved from the *orto-* to the *para-* position, then a mononuclear complex is formed.[6] Thus, the driving force for the formation of a mono- or di-nuclear complex may arise from the hydrogen bonds and the packing requirements, rather than from any intrinsic tendency for Cu(II) to achieve a specific coordination.

The hydrogen atoms bound to the water molecules cannot be accurately determined from available data. The hydrogen bonds listed in Table 4 are therefore proposed from the intermolecular oxygen–oxygen distances. It may be concluded that the structure is held together in the *bc*-plane by hydrogen bonds and in the *a*-direction by van der Waals forces.

All phenyl-groups in the structure are within the limits of error situated in parallel planes. This is achieved by the torsion angles C1–O3–C7–C8 and C11–O8–C17–C18 which are −177.3 and −84.5°, respectively. Another difference between the two crystallographically independent ligands is that only one of the nitro-groups is involved in hydrogen bonding (O11). A slight degree of disorder in the nitrogroups is also indicated by the relatively high thermal parameters (see Table 2). This may explain the differences in bond lengths and bond angles around N1 and N11.

Table 4. Proposed hydrogen bondings (Å).

Ow1–H···O15(i)	3.103(9)
Ow1–H···Ow2(ii)	2.757(10)
Ow2–H···O5(iii)	2.846(9)
Ow2–H···O11(iv)	2.968(12)

Code for superscripts

(i)	$2-x,1-y,1-z$
(ii)	$2-x,-y,1-z$
(iii)	$2-x,-y-1,1-z$
(iv)	$2-x,-y,2-z$

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