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Tetrakis(μ-benzoato-*O*:*O*′)bis(urea)-1κ*O*,2κ*O*-dicopper(II)

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Abstract

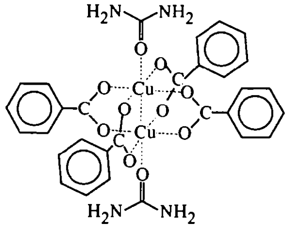
The adduct of tetra-μ-benzoato-dicopper(II) with urea, $[Cu(C_7H_5O_2)_2(CH_4N_2O)]_2$, is dinuclear. Each Cu atom is displaced by 0.195 (3) Å from the plane of the four benzoato O atoms to which it is bonded. The Cu$\cdots$Cu distance is 2.633 (2) Å. The average Cu—O(benzoate) distance is 1.964 (3) Å and the Cu—O(urea) bond length is 2.156 (6) Å.

Comment

Carboxylic acid complexes of copper(II) are of special chemical and biological interest and accordingly have been extensively studied. Their preparation, structural, magnetic and spectral properties have frequently been described (see Melnik, 1982; Kato & Muto, 1988; Valko, Bilton, Morris & Melnik, 1993; Sundberg, Uggla & Melnik, 1996, and references therein). Our interest in copper(II) carboxylates evolves from their biological activity (Bergant, Petrič, Pohleven, Reberšek & Šegedin, 1994; Grgurevič, Petrič, Pohleven & Šegedin, 1996). Different pharmacological effects have been established for solvated mononuclear and dinuclear complexes (Sorensen, 1983) and fungicidal and insecticidal action is to be anticipated.

Several dinuclear tetrabenzoatocopper(II) complexes of general formula $Cu_2(benz)_4.2L$ (benz = $C_6H_5COO^-$; L = axially bonded neutral ligand) have been structurally characterized. The axial ligands L were: methanol, CH_3OH (DAYJIW); dimethylsulfoxide, $(CH_3)_2SO$ (COCYUO); pyridine, C_5H_5N (BZPRCV, BZPRCV01); quinoline, C_9H_7N (TBZOQC); triphenylphosphine oxide, $(C_6H_5)_3PO$ (PILBIV); benzoic acid, C_6H_5COOH (KUBHOE); β-picoline, C_6H_7N (KUBHUK); 4-methylquinoline, $C_{10}H_9N$ (KUBJAS); 7-methylquinoline, $C_{10}H_9N$ (KUBJIA); 4,7-dichloroquinoline, $C_9H_5Cl_2N$ (KUBJOG); caffeine, $C_8H_{10}N_4O_2$ (KUBJUM) (from the Cambridge Structural Database, October 1995 release, with refcodes in parentheses; Allen & Kennard, 1993). Additionally, the dimeric copper(II) benzoate with *N*,*N*-diethylnicotinamide has been described recently (Hökelek, Necefoğlu & Balci, 1995).

In this paper, we report the structure determination of a dinuclear copper(II) benzoate complex with two urea molecules [urea = $CO(NH_2)_2$, CH_4N_2O] acting as axial ligands (Fig. 1), $Cu_2(benz)_4.2(urea)$, (I).



(I)

The structure analysis confirmed the expected dimeric form. Four bidentate benzoate anions form bridges between Cu atoms which have a 4+1 environment. The coordination sphere around each Cu atom is made up of four O atoms of benzoate groups in the basal plane, the apical position being occupied by the urea O atom. The average Cu—O(basal) distance is 1.964 (3) Å, which is a typical value in dimeric copper carboxylates complexes. The Cu atom is shifted by 0.195 (3) Å out of the plane of the four O atoms towards the axial ligand.

As suggested by Kawata *et al.* (1992), $\varphi_{\rm rot}$ (the dihedral angle between the phenyl and carboxyl planes

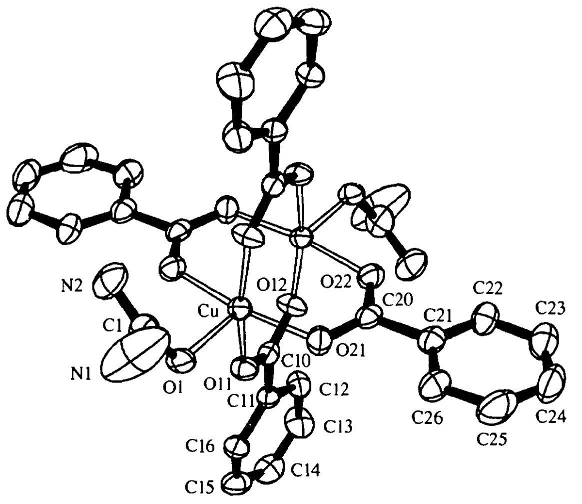


Fig. 1. *ORTEP*II (Johnson, 1971) view of the title molecule with the atomic numbering. Anisotropic displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

in the bridging benzoate ions) and $\varphi_{\rm bend}$ (the dihedral angle between the Cu—O···O—Cu plane and the bridging carboxyl group) were calculated. The values of $\varphi_{\rm rot}$ [9.3 (6) and 3.4 (4)°] and $\varphi_{\rm bend}$ [1.4 (9) and 4.5 (10)°] are a consequence of the molecular packing. For the isolated dimeric complex, these values are expected to be close to zero. Their deviation from zero may also be attributed to the formation of hydrogen bonds of type N—H···O between the urea ligand and the carboxylate groups. The N2 amine group of the urea ligand is linked *via* hydrogen bonds to O atoms of three benzoate groups [N2···O12$^{\rm i}$ 3.10 (1), N2···O22$^{\rm i}$ 3.11 (1) and N2···O11$^{\rm ii}$ 3.20 (2) Å; symmetry codes: (i) $\frac{2}{3}-x$, $\frac{1}{3}-y$, $\frac{1}{3}-z$; (ii) y, $y-x$, $-z$], whereas N1 forms only one weak hydrogen bond [N1···O1$^{\rm iii}$ 3.22 (2) Å; symmetry code: (i) y, $y-x$, $-z$]. This may explain the high thermal motion and possible disorder of N1.

The Cu···Cu distance of 2.633 (2) Å is typical and close to values found in other Cu$^{\rm II}$ benzoates. The carboxyl C—O distances, Cu—Cu—O angles and Cu···Cu distances fit well into the correlation formulae given by Koh & Christoph (1979).

Experimental

The title compound was prepared by the reaction of $CuSO_4.5H_2O$ (0.50 g, 2.0 mmol) in methanol acidified with a few drops of 20% H_2SO_4 with a methanolic solution of sodium benzoate (0.58 g, 4.0 mmol) and urea (0.37 g, 6.2 mmol). After 48 h at room temperature, a blue precipitate was formed. Calculated for Cu_2(benz)$_4$.2(urea): Cu 17.4, C 49.3, H 3.86, N 7.66%; found Cu 17.0, C 49.2, H 3.78, N 7.72%. Owing to decomposition, the crystals were sealed into glass capillaries.

Crystal data

$[Cu_2(C_7H_5O_2)_4(CH_4N_2O)_2]$
$M_r = 731.67$
Trigonal
$R\bar{3}$ (hexagonal axes)
$a = 26.162\,(7)$ Å
$c = 13.633\,(5)$ Å
$V = 8081\,(4)$ Å^3
$Z = 9$
$D_x = 1.353$ Mg m^{-3}
$D_m = 1.33\,(5)$ Mg m^{-3}
D_m measured by flotation in CCl_4/chlorobenzene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}12°$
$\mu = 1.239$ mm^{-1}
$T = 293\,(2)$ K
Hexagonal prism
0.324 × 0.322 × 0.243 mm
Blue

Data collection

Nonius CAD-4 diffractometer
Variable-rate $\theta/2\theta$ scans
Absorption correction: by integration
$T_{\rm min} = 0.69$, $T_{\rm max} = 0.77$
3685 measured reflections
3141 independent reflections
1531 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.034$
$\theta_{\rm max} = 25.01°$
$h = -26 \rightarrow 26$
$k = -31 \rightarrow 31$
$l = -2 \rightarrow 16$
3 standard reflections
frequency: 180 min
intensity decay: 5.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.259$
$S = 0.990$
3099 reflections
208 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.1591P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.029$
$\Delta\rho_{\rm max} = 1.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.69$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.29146 (4)	0.14826 (4)	0.09991 (7)	0.0431 (4)
O11	0.3201 (3)	0.2320 (2)	0.0714 (5)	0.054 (2)
O12	0.3932 (3)	0.2620 (2)	0.1806 (5)	0.060 (2)
C10	0.3649 (4)	0.2716 (4)	0.1162 (6)	0.047 (2)
C11	0.3860 (4)	0.3347 (4)	0.0887 (6)	0.051 (2)
C12	0.4296 (5)	0.3786 (4)	0.1446 (7)	0.064 (3)
C13	0.4495 (5)	0.4384 (4)	0.1215 (9)	0.083 (3)
C14	0.4262 (5)	0.4514 (5)	0.0416 (10)	0.082 (3)
C15	0.3823 (5)	0.4060 (5)	−0.0184 (9)	0.077 (3)
C16	0.3610 (4)	0.3472 (4)	0.0076 (7)	0.057 (2)
O21	0.2408 (3)	0.1515 (3)	0.2028 (4)	0.059 (2)
O22	0.3129 (3)	0.1828 (3)	0.3171 (5)	0.058 (2)
C20	0.2607 (4)	0.1658 (4)	0.2893 (7)	0.051 (2)
C21	0.2184 (4)	0.1638 (4)	0.3690 (7)	0.059 (2)
C22	0.2382 (5)	0.1824 (4)	0.4619 (7)	0.066 (3)
C23	0.1983 (6)	0.1798 (5)	0.5326 (9)	0.086 (4)
C24	0.1419 (7)	0.1593 (6)	0.5117 (11)	0.098 (4)
C25	0.1225 (6)	0.1420 (7)	0.4197 (12)	0.112 (5)
C26	0.1598 (5)	0.1435 (6)	0.3447 (9)	0.082 (3)
O1	0.2227 (3)	0.1074 (3)	−0.0087 (5)	0.057 (2)
C1	0.2078 (5)	0.0584 (5)	−0.0423 (8)	0.077 (3)
N1	0.1515 (6)	0.0183 (7)	−0.0582 (15)	0.237 (12)
N2	0.2435 (5)	0.0395 (4)	−0.0670 (7)	0.090 (3)

Table 2. *Selected geometric parameters (Å, °)*

Cu—O12$^{\mathrm{i}}$	1.961 (6)	O12—C10	1.251 (10)
Cu—O21	1.962 (6)	O21—C20	1.268 (10)
Cu—O22$^{\mathrm{i}}$	1.966 (6)	O22—C20	1.263 (11)
Cu—O11	1.966 (6)	O1—C1	1.226 (12)
Cu—O1	2.156 (6)	C1—N2	1.301 (14)
Cu—Cu$^{\mathrm{i}}$	2.633 (2)	C1—N1	1.33 (2)
O11—C10	1.267 (10)		
O12$^{\mathrm{i}}$—Cu—O21	87.8 (3)	O11—Cu—O1	100.1 (2)
O12$^{\mathrm{i}}$—Cu—O22$^{\mathrm{i}}$	90.8 (3)	O12$^{\mathrm{i}}$—Cu—Cu$^{\mathrm{i}}$	81.4 (2)
O21—Cu—O22$^{\mathrm{i}}$	169.1 (3)	O21—Cu—Cu$^{\mathrm{i}}$	86.9 (2)
O12$^{\mathrm{i}}$—Cu—O11	167.9 (3)	O22$^{\mathrm{i}}$—Cu—Cu$^{\mathrm{i}}$	82.2 (2)
O21—Cu—O11	89.0 (3)	O11—Cu—Cu$^{\mathrm{i}}$	86.8 (2)
O22$^{\mathrm{i}}$—Cu—O11	90.1 (3)	O1—Cu—Cu$^{\mathrm{i}}$	172.6 (2)
O12$^{\mathrm{i}}$—Cu—O1	91.8 (2)	O12—C10—O11	124.9 (8)
O21—Cu—O1	95.6 (3)	O22—C20—O21	126.5 (8)
O22$^{\mathrm{i}}$—Cu—O1	95.2 (3)	C1—O1—Cu	121.7 (6)
Cu—O11—O12—Cu$^{\mathrm{i}}$	−3.0 (3)	Cu—O21—O22—Cu$^{\mathrm{i}}$	0.3 (3)

Symmetry code: (i) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$.

The space group $R\bar{3}$ was deduced from the systematic absences and on the basis of the previous study of the isostructural $Cu_2(benz)_4.4(CH_3OH)$ (Bkouche-Waksman, Bois, Popovitch & L'Haridon, 1980). Its choice was confirmed by the successful refinement. All H atoms were found in the difference electron density map, apart from those of the urea ligand, and were included in the refinement at calculated positions with isotropic displacement parameters $1.5U_{\rm eq}$ of the attached heavy atoms. The final difference synthesis contained a peak of $+1.25\,e\,Å^{-3}$, but we could not interpret it as an additional methanol or water molecule. Additionally, the large thermal displacement parameters of the urea moiety suggest disorder or decomposition of the compound. The rather high value of the final R factor is ascribed to the inferior quality of the crystals. Two sets of diffraction data from two different crystals were collected in Leipzig and in Ljubljana. Results based on the better set are reported here. The sealed crystals exhibited slight decomposition during the data collection. Calculations were performed on a PC 486/16MB.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4-*PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1294). Services for accessing these data are described at the back of the journal.

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Bis(piperazinium) Pentakis(trioxomolybdo)-bis(phenylphosphonate) Dihydrate

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Abstract

The title compound, bis(piperazine-1,4-diylium) bis(phenylphosphonato)-$1\kappa O,2{:}3\kappa^2O',4{:}5\kappa^2O'';1{:}2\kappa^2O,3{:}4\text{-}\kappa^2O',5\kappa O''$-penta-$\mu$-oxo-$1{:}2\kappa^2O;1{:}5\kappa^2O;2{:}3\kappa^2O;3{:}4\kappa^2\text{-}O;4{:}5\kappa^2O$-decaoxo-$1\kappa^2O,2\kappa^2O,3\kappa^2O,4\kappa^2O,5\kappa^2O$-pentamolybdenum(4−) dihydrate, $(C_4H_{12}N_2)_2[Mo_5O_{15}(C_6H_5O_3P)_2].2H_2O$, contains isolated five-unit rings of vertex- and edge-sharing distorted octahedral MoO_6 units, doubly capped by PC_6H_5 entities (as $[PO_3C_6H_5]^{2-}$ phenylphosphonate groups), to result in $[(MoO_3)_5\{(C_6H_5)PO_3\}_2]^{4-}$ {or $[Mo_5P_2O_{21}(C_6H_5)_2]^{4-}$} anions. Doubly protonated piperazinium cations and water molecules complete the structure.