PQQ was purchased from Ube Industries (Tokyo, Japan). PQQ was dissolved in KOH solution and the pH of the solution was then adjusted to 7.0 by the addition of HCl solution. The addition of CH_3CN to the solution yielded the crystals in a few weeks. The density was measured by flotation in CCl_4-$CH_2BrCH_2CH_2Br$. A crystal was sealed in a glass capillary for the collection of the diffraction data. The unit-cell parameters indicated a monoclinic crystal system and systematic absences indicated the space group. Lattice constants were obtained by least-squares refinement. Intensity data were collected with an ω-scan width of $(1.50 + 0.15\tan\theta)°$ and a scan speed of $4.0°$ min^{-1}. Data were corrected for Lorentz and polarization effects and for absorption.

The structure was solved by direct methods using *MULTAN*78 (Main et al., 1978) and refined by block-diagonal least squares using the program *HBLS-V* (Ashida, 1979). Anisotropic thermal parameters were refined for non-H atoms. The positions of the H atoms of PQQ were calculated on the basis of their molecular geometry. Difference Fourier syntheses calculated at intermediate stages of refinement showed maxima consistent with the expected positions of H atoms of water. H atoms were included with isotropic temperature factors in subsequent refinements. All computations were carried out on an ACOS 2020 computer at the Computation Center, Osaka University, and on an ACOS S-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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Dimeric Copper(II) 2-Methyl-2-phenylpropanoate Adducts with Water or 2,6-Lutidine and a Monomeric Copper(II) Triphenylacetate Adduct with 2,6-Lutidine

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Abstract

The structures of diaquatetrakis(μ-2-methyl-2-phenylpropanoato-O:O')dicopper(II), $[Cu(C_{10}H_{11}O_2)_2(H_2O)]_2$ (I), bis(2,6-dimethylpyridine)tetrakis(μ-2-methyl-2-phenylpropanoato-O:O')dicopper(II) benzene solvate, $[Cu(C_{10}H_{11}O_2)_2(C_7H_9N)]_2.C_6H_6$ (II) and *trans*-bis(2,6-dimethylpyridine)bis(triphenylacetato-O,O')copper(II), $[Cu(C_{20}H_{15}O_2)_2(C_7H_9N)_2]$ (III), have been determined by single-crystal X-ray diffraction. (I) and (II) are dinuclear Cu^{II} complexes having cage structures and the coordination geometries around the Cu atoms are square pyramidal in (I) and distorted trigonal bipyramidal in (II). The $Cu\cdots Cu$ distances are 2.589 (1) and 2.907 (1) Å for (I) and (II), respectively. The coordination geometry in the monomeric copper complex (III) is square planar. The $-2J$ values of (I) and (II) are 348 and 310 cm^{-1}, respectively.

Comment

The antiferromagnetic interaction in dimeric copper-(II) carboxylates decreases as the coordination geometry around the Cu atoms is distorted from square pyramidal (SP) toward trigonal bipyramidal (TBP) (Uekusa et al., 1992). The distorted TBP

structure has been observed only for copper(II) tri-chloroacetate complexes (Uekusa *et al.*, 1992, and references therein) and the triphenylacetate complexes [Cu(Ph$_3$CCOO)$_2$(pyridine)]$_2$.C$_6$H$_6$ (Steward *et al.*, 1991), [Cu(Ph$_3$CCOO)$_2$(4-picoline)]$_2$.2C$_7$H$_8$ and [Cu(Ph$_3$CCOO)$_2$(4-picoline)]$_2$.2C$_6$H$_6$ (Yamanaka *et al.*, 1993). The pK_a value of Cl$_3$CCOOH is very low (0.7 in aqueous solution), suggesting a weak Cu—O coordinate-covalent bond. For the Ph$_3$C-COO$^-$ bridge, the bulkiness of the phenyl groups is expected to be a driving force for the deformation of the Cu$_2$(OCO)$_4$ cage in the crystals. Both of these cases involve electronic and/or geometrical factors of the carboxylato bridges. The SP to TBP distortion also may be accomplished by changing the nature of the apical monodentate ligand. In the present study, the 2,6-lutidine ligand was employed to investigate the influence of steric effects on the complex formation and the magnetism of the complex.

In the reaction of 2,6-lutidine with the aqua adducts [Cu(RCOO)$_2$(H$_2$O)]$_2$ (R = Ph$_3$C, Ph$_2$MeC or PhMe$_2$C), a dimeric complex was obtained only when R = PhMe$_2$C (Jury, 1989). The other complexes gave monomeric adducts. The magnetic susceptibilities of the dimeric copper(II) 2-methyl-2-phenylpropanoate complexes, [Cu(PhMe$_2$C-COO)$_2$L]$_2$, were measured for several adducts using the Faraday method over the temparature range 80–300 K, and the −2J values were determined at Saga University: L = H$_2$O (I), −2J = 348 cm^{-1}; L = 2,6-lutidine (II), −2J = 310 cm^{-1}; L = pyridine, −2J = 362 cm^{-1}; L = 2-picoline, −2J = 351 cm^{-1}; L = 3-picoline, −2J = 358 cm^{-1}; L = 4-picoline, −2J = 352 cm^{-1}; L = quinoline, −2J = 353 cm^{-1}. The magentic susceptibilities of (II) were measured with the sample suspended in high-vacuum pump oil NEOVAC MR-100 to protect against efflorescence.

Complex (I) has a center of symmetry between the Cu···Cu axis (Fig. 1). The intermolecular O···O hydrogen-bond distances are 2.885 (3) and 2.995 (3) Å. The average dihedral angle between O—Cu···Cu—O and O—C—O of the bridges, φ_{bend}, is 2.5 (3)°. The abnormally small antiferromagnetic interaction of [Cu(PhCOO)$_2$(quinoline)]$_2$ [−2J = 267 cm^{-1}, mean φ_{bend} = 11.4 (3)°; Kawata, Uekusa *et al.*, 1992] and [Cu(2-Cl-PhCOO)$_2$(H$_2$O)]$_2$ [−2J = 262 cm^{-1}, φ_{bend} = 2.2 (1) and 12.5 (1)°; Kawata, Ohba, Tokii, Muto & Kato, 1992] is attributed to the bending of the carboxylato bridges. The −2J value for the aqua adduct (I) is nearly the same as for the corresponding picoline adducts, suggesting that the intermolecular hydrogen bond in (I) has little, if any, effect on the spin-exchange interaction.

The complex (II) has a twofold axis through the Cu···Cu axis (Fig. 2). The coordination geometry around the Cu atoms is of the distorted TBP type. Within a complex, short contacts are observed
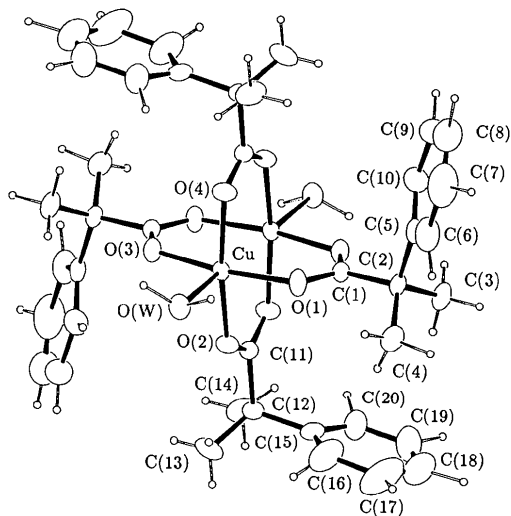

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure of (I) with the thermal ellipsoids scaled at the 25% probability level.

between the methyl groups of the 2,6-lutidine ligands and the O atoms of the carboxylato bridges. Thus, the SP to TBP distortion occurs in the solvated crystal due to the bulkiness of the 2,6-lutidine ligand. The SP structure of the corresponding quinoline adduct has been reported previously in a comparative structural study with the silanecarboxylate complex (Uekusa *et al.*, 1990). The dimensions of the central cage structure of (II) are compared with those of the quinoline adduct in Table 3. The TBP distortion in the 2,6-lutidine adduct (II) is moderate and the average equatorial O—Cu—O bond angle is 144.1 (1)°. In the trichloroacetate complexes, a moderate TBP distortion is observed for the 2,5-dichloropyridine adduct with an average equatorial O—Cu—O bond angle of 145.5 (2)°. The structural data of the 4,7-dichloroquinoline adduct, which is a typical SP structure, are also given in Table 3. A linear correlation between the −2J values and the Cu···Cu distances among the 14 dimeric copper(II) trichloroacetate complexes shows that the inclination ratio Δ(−2J)/Δ(Cu···Cu) is −274 cm^{-1} Å^{-1} with a correlation coefficient of 0.949 (Uekusa *et al.*, 1992). The smaller −2J value of (II) than that of the quinoline adduct agrees with the trend. The −2J value of (II) measured after efflorescence is 337 cm^{-1}, suggesting that the TBP distortion is somewhat relaxed on removal of the benzene of crystallization.

The monomeric complex (III) (Fig. 3) has a center of symmetry at the Cu atom, which is surrounded by two N atoms of two 2,6-lutidine ligands and two O(1) atoms of two triphenylacetato ligands yielding a square-planar arrangement. The molecular structure
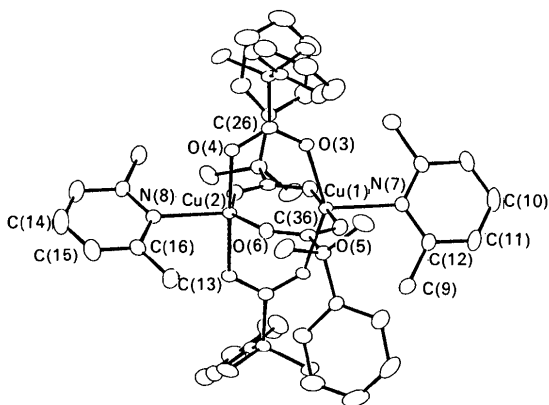
Fig. 2. *ORTEP* drawing (Johnson, 1965) of the molecular structure of (II) with 25% probability ellipsoids. H atoms have been omitted for clarity.

is similar to that of the pyridine adduct (Steward *et al.*, 1991). The Cu—O(2) distance is 2.825 (4) Å, which is longer by 0.889 (4) Å than the Cu—O(1) bond distance. The Cu—N bond distance, 2.048 (4) Å, is only 0.033 (4) Å longer than that of the pyridine adduct. In this monomeric complex, there is enough space around the two methyl groups of the 2,6-lutidine ligand so that steric crowding does not occur.
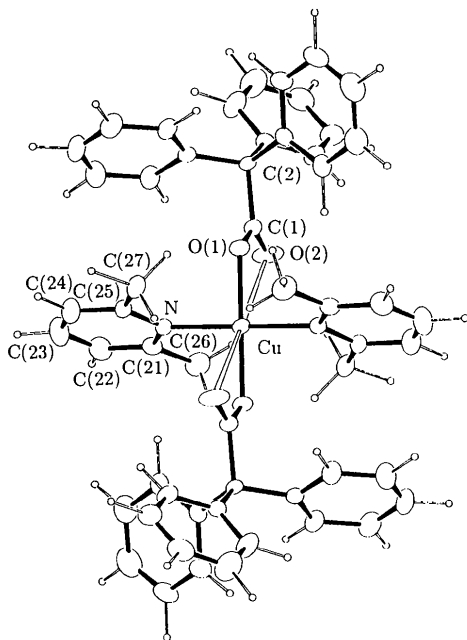

Fig. 3. *ORTEP* drawing (Johnson, 1965) of (III) with 25% probability ellipsoids.

Experimental

Compound (I)

Crystal data

$[Cu_2(C_{10}H_{11}O_2)_4(H_2O)_2]$
$M_r = 815.91$
Triclinic
$P\bar{1}$
$a = 11.782$ (2) Å
$b = 12.524$ (2) Å
$c = 7.041$ (2) Å
$\alpha = 95.49$ (2)°
$\beta = 98.01$ (2)°
$\gamma = 84.71$ (2)°
$V = 1020.8$ (4) Å^3
$Z = 1$

$D_x = 1.33$ Mg m^{-3}
$D_m = 1.33$ (2) Mg m^{-3}
Density measured by flotation in CCl$_4$-*cyclo*-C$_6$H$_{12}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 43 reflections
$\theta = 10$–15°
$\mu = 1.09$ mm^{-1}
$T = 298$ (2) K
Prism
$0.55 \times 0.45 \times 0.20$ mm
Green

Data collection

Rigaku AFC-5 four-circle diffractometer
θ–2θ scans
Absorption correction:
  by integration from crystal shape
  $T_{min} = 0.599$, $T_{max} = 0.795$
6385 measured reflections
5937 independent reflections
4584 observed reflections
  $[|F_o| > 3\sigma(|F_o|)]$

$R_{int} = 0.011$
$\theta_{max} = 30.0°$
$h = -16 \rightarrow 16$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 9$
5 standard reflections
  monitored every 100 reflections
  intensity variation:
  0.964–1.020%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.054$
$S = 1.94$
4584 reflections
332 parameters
All H-atom parameters refined

$w = [\sigma^2(|F_o|) + (0.015|F_o|)^2]^{-1}$
$(\Delta/\sigma)_{max} = 0.28$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$[Cu_2(C_{10}H_{11}O_2)_4(C_7H_9N)_2]$.-$C_6H_6$
$M_r = 1072.30$
Monoclinic
$C2/c$
$a = 13.033$ (1) Å
$b = 22.608$ (3) Å
$c = 16.703$ (1) Å
$\beta = 90.76$ (1)°
$V = 4920.9$ (8) Å^3
$Z = 4$

$D_x = 1.38$ Mg m^{-3}
$D_m = 1.35$ (2) Mg m^{-3}
Density measured by flotation in CCl$_4$-*cyclo*-C$_6$H$_{12}$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 39 reflections
$\theta = 10$–15°
$\mu = 0.92$ mm^{-1}
$T = 298$ (2) K
Prism
$0.55 \times 0.40 \times 0.30$ mm
Green

Data collection

Rigaku AFC-5 four-circle
    diffractometer
θ–2θ scans
Absorption correction:
    by integration from crystal
    shape
    T_{min} = 0.713, T_{max} =
    0.715
11 523 measured reflections
5650 independent reflections
3395 observed reflections
    $[|F_o| > 3\sigma(|F_o|)]$

R_{int} = 0.020
θ_{max} = 27.5°
h = -16 → 16
k = -26 → 26
l = -21 → 0
4 standard reflections
    monitored every 100
    reflections
    intensity variation:
    0.968-1.128%

Refinement

Refinement on F
R = 0.047
wR = 0.041
S = 1.57
3395 reflections
300 parameters
H-atom parameters not re-
    fined

$w = [\sigma^2(|F_o|)$
    $+ (0.015|F_o|)^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.25
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = -0.29 e Å^{-3}
Atomic scattering factors
    from International Tables
    for X-ray Crystallography
    (1974, Vol. IV)

Compound (III)

Crystal data

[Cu(C$_{20}$H$_{15}$O$_2$)$_2$(C$_7$H$_9$N)$_2$]
M_r = 852.53
Monoclinic
$P2_1/n$
a = 19.928 (4) Å
b = 10.982 (2) Å
c = 10.017 (2) Å
β = 97.98 (2)°
V = 2171.0 (7) Å^3
Z = 2

D_x = 1.30 Mg m^{-3}
D_m = 1.29 (2) Mg m^{-3}
Density measured by flota-
    tion in CCl$_4$-CH$_2$ClCH$_2$Cl
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24
    reflections
θ = 10- 15°
μ = 0.55 mm^{-1}
T = 300 (2) K
Needle
0.50 × 0.18 × 0.12 mm
Violet

Data collection

Rigaku AFC-5 four-circle
    diffractometer
θ–2θ scans
Absorption correction:
    by integration from crystal
    shape
    T_{min} = 0.894, T_{max} =
    0.944
5268 measured reflections
4986 independent reflections
2228 observed reflections
    $[|F_o| > 3\sigma(|F_o|)]$

R_{int} = 0.024
θ_{max} = 27.5°
h = -25 → 25
k = 0 → 14
l = 0 → 13
5 standard reflections
    monitored every 100
    reflections
    intensity variation:
    0.964-1.020%

Refinement

Refinement on F
R = 0.056
wR = 0.054

$w = [\sigma^2(|F_o|)$
    $+ (0.015|F_o|)^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.23

S = 1.61
2228 reflections
281 parameters
H-atom parameters not re-
    fined

$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = -0.47 e Å^{-3}
Atomic scattering factors
    from International Tables
    for X-ray Crystallography
    (1974, Vol. IV)

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Compound (I)				
Cu	0.04106 (3)	0.02864 (2)	-0.14696 (4)	2.7
O(1)	0.0201 (2)	-0.1199 (1)	-0.2552 (3)	4.0
O(2)	0.1877 (2)	-0.0221 (2)	-0.0046 (3)	4.0
O(3)	0.0438 (2)	0.1698 (1)	-0.0023 (3)	3.8
O(4)	-0.1201 (2)	0.0677 (2)	-0.2517 (3)	4.0
O(W)	0.1153 (2)	0.0754 (2)	-0.3829 (3)	4.2
C(1)	-0.0152 (2)	-0.1887 (2)	-0.1627 (4)	3.0
C(2)	-0.0244 (2)	-0.3028 (2)	-0.2636 (4)	3.6
C(3)	-0.0132 (3)	-0.3850 (2)	-0.1139 (5)	5.3
C(4)	0.0736 (3)	-0.3285 (3)	-0.3869 (6)	6.1
C(5)	-0.1432 (3)	-0.3037 (2)	-0.3816 (5)	4.1
C(6)	-0.1559 (4)	-0.3351 (3)	-0.5783 (6)	7.2
C(7)	-0.2653 (5)	-0.3366 (4)	-0.6802 (8)	12.1
C(8)	-0.3610 (4)	-0.3116 (4)	-0.5935 (10)	12.3
C(9)	-0.3490 (4)	-0.2774 (4)	-0.4026 (10)	10.2
C(10)	-0.2386 (3)	-0.2734 (3)	-0.2981 (7)	6.5
C(11)	0.1997 (2)	-0.0595 (2)	0.1560 (4)	3.3
C(12)	0.3219 (2)	-0.1021 (2)	0.2397 (5)	4.2
C(13)	0.4119 (3)	-0.0482 (4)	0.1548 (8)	7.9
C(14)	0.3403 (3)	-0.0748 (3)	0.4557 (6)	6.7
C(15)	0.3299 (2)	-0.2234 (3)	0.1863 (5)	5.1
C(16)	0.3587 (5)	-0.2679 (4)	0.0162 (8)	9.6
C(17)	0.3697 (6)	-0.3825 (5)	-0.0269 (9)	13.3
C(18)	0.3462 (4)	-0.4418 (4)	0.1063 (10)	11.9
C(19)	0.3138 (5)	-0.4028 (4)	0.2702 (12)	12.3
C(20)	0.3053 (4)	-0.2942 (3)	0.3114 (10)	10.0
Compound (II)				
Cu(1)	0.0	0.08113 (3)	0.25	2.3
Cu(2)	0.0	0.20971 (3)	0.25	2.3
O(3)	-0.1432 (2)	0.1095 (1)	0.2117 (1)	2.9
O(4)	-0.1404 (2)	0.2083 (1)	0.2142 (1)	2.7
O(5)	0.0438 (2)	0.0825 (1)	0.1412 (1)	3.1
O(6)	0.0432 (2)	0.1814 (1)	0.1368 (1)	3.0
N(7)	0.0	-0.0200 (2)	0.25	2.7
N(8)	0.0	0.3117 (2)	0.25	2.6
C(9)	0.1828 (3)	-0.0172 (2)	0.2231 (3)	5.0
C(10)	0.0	-0.1434 (3)	0.25	5.1
C(11)	0.0884 (3)	-0.1122 (2)	0.2364 (2)	4.2
C(12)	0.0870 (3)	-0.0509 (2)	0.2365 (2)	3.1
C(13)	0.1382 (3)	0.3094 (2)	0.1516 (2)	4.3
C(14)	0.0	0.4347 (3)	0.25	6.4
C(15)	0.0662 (4)	0.4036 (2)	0.2023 (3)	5.0
C(16)	0.0658 (3)	0.3425 (2)	0.2033 (2)	3.1
C(17)	-0.2549 (3)	0.1163 (2)	0.0426 (2)	4.4
C(18)	-0.2632 (4)	0.1134 (2)	-0.0401 (3)	5.8
C(19)	-0.3173 (3)	0.1560 (2)	-0.0824 (2)	5.2
C(20)	-0.3618 (3)	0.2017 (2)	-0.0420 (3)	4.8
C(21)	-0.3546 (3)	0.2045 (2)	0.0414 (2)	3.6
C(22)	-0.3016 (2)	0.1614 (2)	0.0847 (2)	2.7
C(23)	-0.3545 (3)	0.1055 (2)	0.2067 (2)	3.9
C(24)	-0.3479 (3)	0.2161 (2)	0.2133 (2)	4.3
C(25)	-0.2984 (2)	0.1608 (2)	0.1765 (2)	2.6
C(26)	-0.1843 (2)	0.1587 (2)	0.2033 (2)	2.5
C(27)	0.2790 (3)	0.1532 (2)	0.0605 (2)	4.0
C(28)	0.3841 (3)	0.1422 (2)	0.0657 (3)	5.4
C(29)	0.4224 (4)	0.0903 (3)	0.0386 (3)	6.5
C(30)	0.3583 (4)	0.0487 (2)	0.0062 (4)	6.6
C(31)	0.2519 (4)	0.0591 (2)	0.0003 (3)	4.9
C(32)	0.2116 (3)	0.1119 (2)	0.0266 (2)	2.8
C(33)	0.0361 (3)	0.0795 (2)	-0.0249 (2)	4.8
C(34)	0.0839 (3)	0.1866 (2)	-0.0239 (2)	4.4

C(35)	0.0976 (3)	0.1277 (2)	0.0196 (2)	2.8
C(36)	0.0572 (2)	0.1318 (2)	0.1066 (2)	2.6

Compound (III)

Cu	0.0	0.0	0.0	2.8
O(1)	−0.0498 (2)	0.1510 (3)	0.0041 (3)	3.4
O(2)	−0.1229 (2)	0.0441 (3)	0.1023 (4)	5.9
N	0.0507 (2)	0.0395 (3)	0.1870 (4)	3.0
C(1)	−0.1032 (2)	0.1397 (4)	0.0607 (5)	3.2
C(2)	−0.1408 (2)	0.2630 (4)	0.0763 (5)	2.9
C(3)	−0.1642 (2)	0.3184 (4)	−0.0635 (5)	3.2
C(4)	−0.1934 (3)	0.4352 (5)	−0.0726 (6)	4.9
C(5)	−0.2168 (3)	0.4840 (5)	−0.1982 (7)	7.0
C(6)	−0.2116 (3)	0.4186 (6)	−0.3135 (7)	7.3
C(7)	−0.1848 (3)	0.3051 (6)	−0.3057 (6)	6.3
C(8)	−0.1609 (3)	0.2559 (5)	−0.1823 (5)	4.4
C(9)	−0.0868 (2)	0.3398 (4)	0.1643 (5)	3.4
C(10)	−0.0575 (3)	0.4434 (5)	0.1183 (5)	4.2
C(11)	−0.0054 (3)	0.5035 (6)	0.2022 (6)	5.5
C(12)	0.0182 (3)	0.4593 (5)	0.3270 (6)	6.1
C(13)	−0.0099 (3)	0.3564 (6)	0.3719 (6)	6.4
C(14)	−0.0614 (3)	0.2969 (5)	0.2920 (5)	5.1
C(15)	−0.2052 (2)	0.2434 (4)	0.1444 (5)	3.2
C(16)	−0.2523 (3)	0.1584 (5)	0.0922 (6)	4.4
C(17)	−0.3116 (3)	0.1407 (5)	0.1478 (6)	5.3
C(18)	−0.3249 (3)	0.2115 (6)	0.2527 (6)	5.6
C(19)	−0.2808 (3)	0.3004 (7)	0.3000 (6)	7.4
C(20)	−0.2203 (3)	0.3159 (6)	0.2475 (6)	6.0
C(21)	0.0425 (2)	−0.0296 (4)	0.2953 (5)	3.5
C(22)	0.0784 (3)	−0.0071 (6)	0.4203 (5)	5.2
C(23)	0.1239 (3)	0.0878 (7)	0.4359 (6)	6.6
C(24)	0.1312 (3)	0.1604 (6)	0.3271 (6)	5.6
C(25)	0.0942 (2)	0.1350 (5)	0.2027 (5)	3.7
C(26)	−0.0066 (3)	−0.1307 (5)	0.2741 (5)	4.9
C(27)	0.1022 (3)	0.2115 (5)	0.0841 (5)	4.4

Table 2. Selected bond lengths (Å) and angles (°)

Compound (I)

Cu···Cuⁱ	2.589 (1)	O(1)—C(1)	1.260 (3)
Cu—O(1)	1.966 (1)	O(2)—C(11)	1.250 (4)
Cu—O(2)	1.957 (2)	O(3)—C(1ⁱ)	1.249 (4)
Cu—O(3)	1.955 (1)	O(4)—C(11ⁱ)	1.245 (4)
Cu—O(4)	1.974 (2)	O(W)···O(1ⁱⁱ)	2.885 (3)
Cu—O(W)	2.134 (3)	O(W)···O(4ⁱⁱ)	2.995 (3)

O(1)—Cu—O(2)	89.1 (1)	O(3)—Cu—O(W)	95.2 (1)
O(1)—Cu—O(3)	168.9 (1)	O(4)—Cu—O(W)	96.0 (1)
O(1)—Cu—O(4)	88.3 (1)	Cu—O(1)—C(1)	122.5 (2)
O(1)—Cu—O(W)	95.7 (1)	Cu—O(2)—C(11)	125.3 (2)
O(2)—Cu—O(3)	91.9 (1)	Cu—O(3)—C(1ⁱ)	123.8 (2)
O(2)—Cu—O(4)	168.9 (1)	Cu—O(4)—C(11ⁱ)	120.6 (2)
O(2)—Cu—O(W)	95.0 (1)	O(1)—C(1)—O(3ⁱ)	116.8 (2)
O(3)—Cu—O(4)	88.6 (1)	O(2)—C(11)—O(4ⁱ)	125.0 (2)

Compound (II)

Cu(1)···Cu(2)	2.907 (1)	Cu(2)—N(8)	2.306 (4)
Cu(1)—O(3)	2.067 (2)	O(3)—C(26)	1.243 (4)
Cu(1)—O(5)	1.912 (2)	O(4)—C(26)	1.270 (4)
Cu(1)—N(7)	2.287 (4)	O(5)—C(36)	1.269 (4)
Cu(2)—O(4)	1.918 (4)	O(6)—C(36)	1.246 (4)
Cu(2)—O(6)	2.081 (2)		

O(3)—Cu(1)—O(5)	88.9 (1)	O(6)—Cu(2)—N(8)	107.9 (1)
O(3)—Cu(1)—N(7)	108.0 (1)	O(6)—Cu(2)—O(6ⁱⁱⁱ)	144.2 (1)
O(3)—Cu(1)—O(3ⁱⁱⁱ)	143.9 (1)	Cu(1)—O(3)—C(26)	134.3 (2)
O(5)—Cu(1)—N(7)	90.9 (1)	Cu(2)—O(4)—C(26)	119.1 (2)
O(5)—Cu(1)—O(5ⁱⁱⁱ)	178.2 (1)	Cu(1)—O(5)—C(36)	119.5 (2)
O(4)—Cu(2)—O(6)	88.9 (1)	Cu(2)—O(6)—C(36)	133.5 (2)
O(4)—Cu(2)—N(8)	91.0 (1)	O(3)—C(26)—O(4)	125.6 (3)
O(4)—Cu(2)—O(4ⁱⁱⁱ)	178.0 (1)	O(5)—C(36)—O(6)	125.8 (3)

Compound (III)

Cu—O(1)	1.936 (3)	O(1)—C(1)	1.279 (5)
Cu—O(2)	2.825 (4)	O(2)—C(1)	1.215 (6)
Cu—N	2.048 (4)		

O(1)—Cu—O(2)	51.1 (1)	Cu—O(1)—C(1)	112.7 (3)
O(1)—Cu—N	89.3 (1)	Cu—O(2)—C(1)	71.7 (3)
O(2)—Cu—N	88.5 (1)	O(1)—C(1)—O(2)	124.3 (4)

Symmetry codes: (i) −x, −y, −z; (ii) −x, −y, 1 − z; (iii) −x, y, ½ − z.

Table 3. Comparison of the dimensions (Å, °) of the Cu₂(COO)₄ cage in [Cu(RCOO)₂L]₂S and their −2J values

	R = PhMe₂C L = quinoline S = none	PhMe₂C 2,6-lutidine benzene	Cl₃C 4,7-Cl₂-quinoline none	Cl₃C 2,5-Cl₂-pyridine none
Cu···Cu (Å)	2.683 (1)	2.907 (1)	2.786 (1)	2.951 (1)
Cu—O_{min}	1.963 (2)	1.912 (2)	1.963 (3)	1.932 (4)
Cu—O_{max}	1.994 (2)	2.081 (2)	1.981 (3)	2.130 (4)
Cu—L	2.220 (2)	2.287 (4) 2.306 (4)	2.161 (4)	2.120 (5)
Cu—O—C_{min} (°)	120.3 (2)	119.1 (2)	119.2 (3)	115.2 (3)
Cu—O—C_{max}	127.9 (2)	134.3 (2)	127.7 (3)	133.8 (4)
O—Cu—O_{trans}	166.5 (1) 166.8 (1)	178.0 (1) 178.2 (1)	163.8 (1) 163.9 (1)	173.5 (2) 174.4 (2)
O—Cu—O_{eq}		143.9 (1) 144.2 (1)		145.4 (2) 145.6 (2)
Structural type	SP	Distorted TBP	SP	Distorted TBP
−2J (cm⁻¹)	353	310	237	191
Reference	(a)	(b)	(c)	(c)

References: (a) Uekusa *et al.* (1990); (b) this work; (c) Uekusa *et al.* (1992).

The compounds [Cu(PhMe₂CCOO)₂(H₂O)]₂ (I) and [Cu(Ph₃C-COO)₂(H₂O)]₂ (IV) were prepared as reported previously (Steward *et al.*, 1986). To the benzene solutions of these aqua adducts, 2,6-lutidine was added to yield compounds (II) and (III). For (II), 1.0 g (1.2 mmol) of (I) was dissolved in 50 ml of benzene. On addition of 2,6-lutidine (0.26 g, 2.4 mmol) the color of the solution changed from blue-green to green. Addition of petroleum ether (100 ml) yielded a green precipitate which was separated by filtration, washed with benzene-petroleum ether (10:90 v/v) and air dried. For (III), 0.21 g (0.31 mmol) of (IV) was dissolved in 25 ml of benzene. On dropwise addition of 2,6-lutidine (0.10 g, 0.93 mmol), the color of the solution changed from blue-green to lavender and a lavender precipitate formed. The precipitate was collected by filtration, washed with benzene-petroleum ether (70:30 v/v) and air dried.

For compound (I), 19 H atoms out of 24 were located on difference Fourier syntheses, and the others were calculated. Crystal-structure analysis of [Cu(PhMe₂CCOO)₂-(pyridine)]₂ was attempted but not carried out because two independent dimers exist in the crystals and a sufficient number of reflections could not be collected: monoclinic, $P2_1/m$, $a = 41.925$ (6), $b = 20.519$ (5), $c = 10.841$ (2) Å, $\beta = 92.46$ (1)°, $V = 9317$ (3) Å³, $Z = 8$, $D_m = 1.34$ (2), $D_x = 1.34$ Mg m⁻³.

For compound (II), the specimen was coated with adhesive to prevent efflorescence. All the H atoms were located on difference Fourier syntheses. The benzene molecules were not located on the difference Fourier syntheses; rather, the density and efflorescence of the crystals in air indicated the presence of the benzene of crystallization.

For compound (III), it was predicted that the molecule has a crystallographic center of symmetry. Three H atoms out of 24 were located on difference Fourier syntheses and the others were calculated.

Calculations for (I) and (III) were performed using *UNICS*III (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University. Calculations for (II) were performed using *CRYSTAN-GM* (MAC Science, 1992) on a SUN SPARC2 workstation.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71358 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1036]

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Structure of Hexaaquacobalt Hydrogen Phthalate

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Abstract

The structure of $[Co(H_2O)_6](C_8H_5O_4)_2$ consists of octahedrally coordinated cobalt cations with a mean Co—O distance of 2.091 (10) Å. Anion–anion and anion–water hydrogen bonding is observed.

Comment

We have reported elsewhere on the crystal structures of various magnesium hydrogen phthalates (Kariuki & Jones, 1989, 1990, 1992). Our principal aim has been to understand the structural influences involved in the decomposition of peracid salts, as well as the relationship between the solid intermediates observed during decomposition – some of these were amorphous. One of the phases generated during decomposition could not be obtained in a form suitable for single-crystal studies. The structure of the cobalt analogue, however, has been determined and is reported here. The powder X-ray patterns and the computer simulation of the patterns confirm that the structures are identical.

The structure consists of cobalt cations, water molecules and hydrogen phthalate anions (I).

(I)
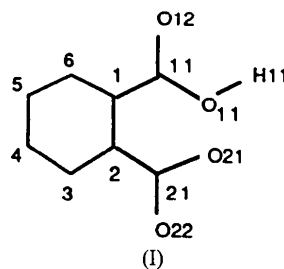
The Co^{2+} cations occupy centres of symmetry. Each Co atom is coordinated to six molecules of water in the form of an octahedron with a mean Co—O distance of 2.091 (10) Å. There are two anions per cation. In the carboxylate group, the two C—O bond lengths are very similar [mean = 1.257 (10) Å]. The maximum deviation from the least-squares plane of the benzene ring is 0.0098 Å [C(5)]. The dihedral angle between the plane through the carboxylate group [O(21)—C(21)—O(22)] and the ring is 71.8°. The carboxylic group [O(11)—C(11)—O(12)] lies almost in the plane of the ring (dihedral angle = 7.0°), while the planes through the two carboxyl groups are at 72.2° to each other. The torsion angle H(11)—O(11)—C(11)—O(12) is −4.1°.

The crystal structure is composed of layers of ions parallel to the (001) plane (Fig. 1). In the structure, double layers of anions alternate with those of the hydrated cations, $[Co(H_2O)_6]^{2+}$.

Bonds of the types (*a*) anion–anion and (*b*) anion–water are found in the crystal. Bonds of the latter type result in the formation of [anion–$Co(H_2O)_6^{2+}$–anion] 'sandwiches'. The anion–anion hydrogen bonding occurs between carboxylic and carboxylate groups of neighbouring ions, forming chains parallel to the *a* axis.

Similar hydrogen-bonding contacts and crystal-packing features are observed in another polymorph of hexaaquacobalt hydrogen phthalate (Adiwidjaja, Rossmanith & Küppers, 1978). These two crystal forms fall in the class of hydrogen phthalates displaying 'sandwich' packing (Kariuki & Jones, 1992).