

Table 2. Geometric parameters (Å, °)

Ru—Cl	2.3944 (21)	Ru—P(2)	2.3421 (22)
Ru—C(1)	2.259 (5)	P(1)—C(1M)	1.834 (7)
Ru—C(2)	2.236 (5)	P(1)—C(111)	1.832 (5)
Ru—C(3)	2.227 (5)	P(1)—C(121)	1.837 (5)
Ru—C(4)	2.240 (5)	P(2)—C(2M)	1.831 (10)
Ru—C(5)	2.263 (5)	P(2)—C(3M)	1.792 (10)
Ru—C(6)	2.273 (5)	P(2)—C(211)	1.831 (5)
Ru—P(1)	2.3509 (18)		
Cl—Ru—P(1)	88.36 (7)	P(1)—C(111)—C(116)	123.5 (3)
Cl—Ru—P(2)	88.83 (7)	P(1)—C(121)—C(122)	117.9 (4)
P(1)—Ru—P(2)	92.29 (7)	P(1)—C(121)—C(126)	122.0 (4)
Ru—P(1)—C(1M)	116.49 (22)	Ru—P(2)—C(2M)	113.9 (3)
Ru—P(1)—C(111)	111.90 (16)	Ru—P(2)—C(3M)	121.3 (3)
Ru—P(1)—C(121)	115.15 (17)	Ru—P(2)—C(211)	111.36 (18)
C(1M)—P(1)—C(111)	100.4 (3)	C(2M)—P(2)—C(3M)	102.3 (5)
C(1M)—P(1)—C(121)	106.0 (3)	C(2M)—P(2)—C(211)	103.8 (4)
C(111)—P(1)—C(121)	105.27 (22)	C(3M)—P(2)—C(211)	102.3 (4)
P(1)—C(1M)—C(1M')	114.8(5)	P(2)—C(211)—C(212)	119.3 (4)
P(1)—C(111)—C(112)	116.3 (3)	P(2)—C(211)—C(216)	120.7 (4)

C(1M') is related to C(1M) by inversion through (0, 0, $\frac{1}{2}$).

The title compound was prepared by mixing [(C₆H₆)(Me₂PPh)-RuCl₂] and dppe (2:1 molar ratio) in CH₂Cl₂/MeOH (5:1 v/v) in the presence of NH₄PF₆; crystals were grown from MeNO₂/MeOH. The crystal was pre-aligned using oscillation and Weissenberg photography and mounted with the *b* axis parallel to the spindle of the two-circle instrument. The ω -scan width was [1.0 + 0.5(sin μ /tan θ)]°. The structure was solved and refined using *SHELX76* (Sheldrick, 1976). The metal position was deduced from a Patterson synthesis and the remaining non-H atoms located by subsequent refinement and ΔF synthesis. Refinement was by full-matrix least squares. Disorder in the PF₆⁻ anion was modelled by allowing split occupancies for four of the F atoms.

Fig. 1 was produced using an interactive version of *ORTEP*II (Mallinson & Muir, 1985) and molecular-geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

We thank the SERC for support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55372 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1003]

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Dimeric Copper(II) 2,2-Dimethylpropanoate Adducts with 3- or 4-Picoline

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Abstract

The structures of tetrakis(μ -2,2-dimethylpropanoate-*O,O'*)-bis(3- or 4-picoline)dicopper(II) benzene solvate, [Cu{(CH₃)₂CCOO}₂C₆H₇N]₂·C₆H₆, have been determined by single-crystal X-ray diffraction. The binuclear Cu^{II} complexes have a cage structure with a square-pyramidal coordination geometry around the Cu atoms. The Cu...Cu distances are 2.657 (3) and 2.648 (5) Å for 3- and 4-picoline adducts, respectively. In the crystal, benzene molecules are accommodated statistically in a hollow running along the *c* axis. The magneto-structural correlation could not be determined because of the easy removal of the benzene molecules from the crystals under the reduced pressure conditions at which the magnetic susceptibility measurements were made.

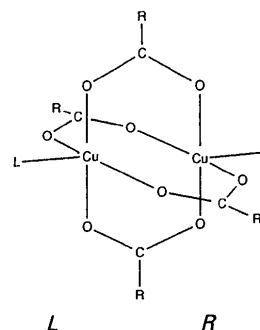
Comment

The magnetic properties of dimeric copper(II) 2,2-dimethylpropanoate complexes were reported by Muto, Hirashima, Tokii, Kato & Suzuki (1986), and some of them were remeasured later by one of the authors (TT). An unexpectedly small $-2J$ value (325 cm⁻¹) was observed for the 4-picoline adduct compared with related compounds (pyridine 368 cm⁻¹, 2- and 3-picoline adducts 372 and 363 cm⁻¹ respectively). The smaller $-2J$ value of the 4-picoline adduct was tentatively attributed to the higher basicity of the 4-picoline compared with other similar ligands (Muto *et al.*, 1986). However, the $-2J$ values of the 2-, 3- and 4-picoline adducts of

the dimeric copper(II) acetates are almost the same ($-2J = 332, 326$ and 333 cm^{-1} respectively; Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Tokii, Muto & Steward, 1991). It is expected that the reduction of the $-2J$ value of the 4-picoline adduct of the dimeric copper(II) 2,2-dimethylpropanoate may be attributed to some deformation of the molecular structure in the crystal. Unfortunately, the present study could not give any answer to this problem because the magnetic susceptibility measurements were only made on samples which had lost benzene from the crystal under reduced pressure. The benzene molecules were not located on the difference syntheses although the density and efflorescence of the crystals indicated the presence of benzene which may be distributed randomly in the hollow (see Fig. 2).

The structures of the binuclear complexes are shown in Fig. 1. The complex with 3-picoline (I) has a twofold axis perpendicular to the $\text{Cu}\cdots\text{Cu}$ axis, and that with 4-picoline (II) has crystallographic $2/m$ symmetry with the twofold axis through the $\text{Cu}\cdots\text{Cu}$

axis. The crystal structures are shown in Fig. 2. The arrangement of the complexes in both crystals is quite unique with the picoline ligands stacked nearly parallel to each other along the c axis. The cell parameter c in (I) and (II) [$11.303(2)$ and $11.111(2) \text{ \AA}$ respectively] is therefore roughly six times the van der Waals radius of the aromatic C atom (1.77 \AA).



L	R
(I) 3-Picoline	Me_3C
(II) 4-Picoline	Me_3C

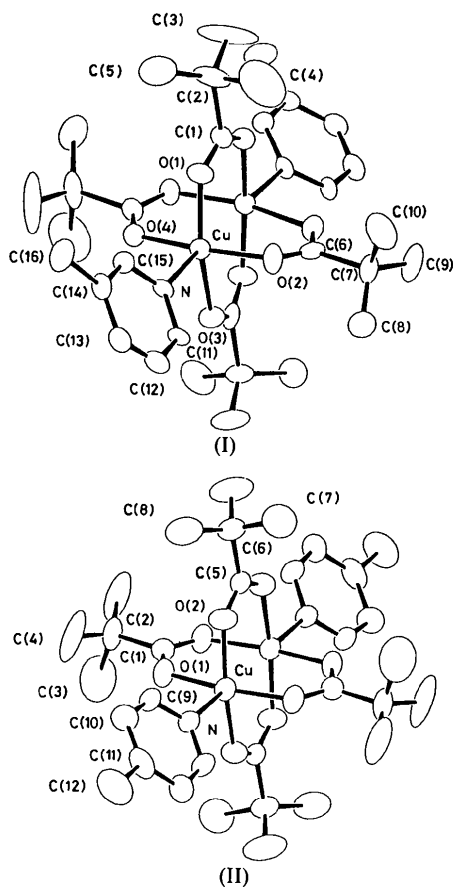


Fig. 1. ORTEP drawings (Johnson, 1965) of the molecular structures with the thermal ellipsoids scaled at the 25% probability level.

The atomic coordinates are listed in Table 1, and selected bond lengths and bond angles in Table 2.

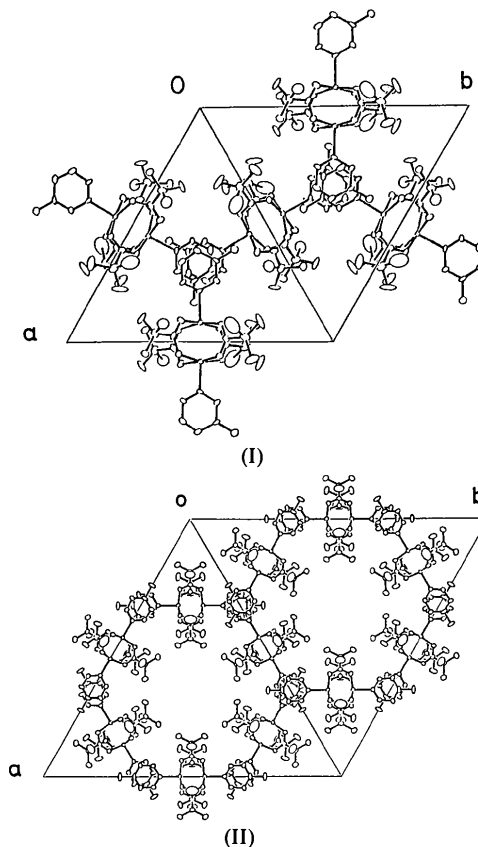
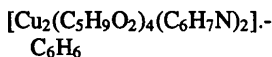


Fig. 2. Projections of the crystal structures along the c axis.

Experimental**Compound (I)***Crystal data* $M_r = 795.64$

Trigonal

 $P3_121$ (or $P3_221$) $a = 18.246$ (2) Å $c = 11.303$ (2) Å $V = 3258.7$ (7) Å³ $Z = 3$ $D_x = 1.22$ Mg m⁻³ $D_m = 1.22$ (2) Mg m⁻³*Data collection*

Rigaku AFC-5 four-circle diffractometer

 θ -2 θ scans

Absorption correction:

by integration from crystal shape

 $T_{\min} = 0.711$, $T_{\max} = 0.779$

2816 measured reflections

2685 independent reflections

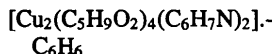
1420 observed reflections

 $[|F_o| > 3\sigma(|F_o|)]$ *Refinement*Refinement on F Final $R = 0.077$ $wR = 0.105$ $S = 3.50$

1420 reflections

200 parameters

H-atom parameters not refined

Compound (II)*Crystal data* $M_r = 795.64$

Rhombohedral (hexagonal setting)

 $R\bar{3}m$ $a = 31.902$ (4) Å $c = 11.111$ (2) Å $V = 9793$ (3) Å³ $Z = 9$ $D_x = 1.21$ Mg m⁻³*Data collection*

Rigaku AFC-5 four-circle diffractometer

 θ -2 θ scansMo $K\alpha$ radiation $\lambda = 0.71073$ Å

Cell parameters from 20 reflections

 $\theta = 10$ -15° $\mu = 1.02$ mm⁻¹ $T = 300$ (2) K

Prism

0.45 × 0.40 × 0.25 mm

Green

 $R_{\text{int}} = 0.017$ $\theta_{\text{max}} = 27.5^\circ$ $h = 0 \rightarrow 25$ $k = 0 \rightarrow 25$ $l = 0 \rightarrow 13$

5 standard reflections

monitored every 100 reflections

intensity variation: 2.8%

 $w = [\sigma^2(F_o) + (0.015F_o)^2]^{-1}$ $(\Delta/\sigma)_{\text{max}} = 0.36$ $\Delta\rho_{\text{max}} = 0.73$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) $D_m = 1.20$ (2) Mg m⁻³Mo $K\alpha$ radiation $\lambda = 0.71073$ Å

Cell parameters from 19 reflections

 $\theta = 10$ -15° $\mu = 1.02$ mm⁻¹ $T = 300$ (2) K

Prism

0.50 × 0.40 × 0.30 mm

Green

 $R_{\text{int}} = 0.050$ $\theta_{\text{max}} = 25.0^\circ$ $h = 0 \rightarrow 37$

Absorption correction:

by integration from crystal shape

 $T_{\min} = 0.493$, $T_{\max} = 0.708$

2370 measured reflections

2245 independent reflections

905 observed reflections

 $[|F_o| > 3\sigma(|F_o|)]$ *Refinement*Refinement on F Final $R = 0.072$ $wR = 0.094$ $S = 3.51$

905 reflections

146 parameters

H-atom parameters not refined

 $w = [\sigma^2(F_o) + (0.015F_o)^2]^{-1}$ $k = 0 \rightarrow 37$ $l = 0 \rightarrow 13$

5 standard reflections

monitored every 100 reflections

intensity variation: 19.7%

 $(\Delta/\sigma)_{\text{max}} = 0.36$ $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

(I)	$B_{\text{eq}} = (4/3)\sum_i \beta_{ij} a_i \cdot a_j$			B_{eq}
	x	y	z	
Cu	0.4555 (1)	0.5386 (1)	0.0179 (2)	3.9
O(1)	0.3795 (7)	0.4571 (7)	-0.1007 (10)	4.9
O(2)	0.5239 (7)	0.6168 (8)	-0.1104 (10)	6.0
O(3)	0.5537 (7)	0.6054 (7)	0.1293 (10)	5.4
O(4)	0.3966 (7)	0.4556 (7)	0.1383 (10)	5.1
N	0.3906 (9)	0.6091 (9)	0.0527 (10)	3.9
C(1)	0.3952 (11)	0.4084 (11)	-0.1528 (13)	4.8
C(2)	0.3197 (15)	0.3398 (17)	-0.2374 (19)	9.4
C(3)	0.3398 (24)	0.2663 (20)	-0.2672 (31)	18.1
C(4)	0.3431 (27)	0.4143 (35)	-0.3582 (22)	22.5
C(5)	0.2289 (15)	0.3169 (24)	-0.1943 (34)	19.2
C(6)	0.5859 (11)	0.6128 (10)	-0.1492 (14)	5.0
C(7)	0.6493 (12)	0.6855 (13)	-0.2330 (16)	6.9
C(8)	0.7283 (13)	0.6785 (15)	-0.2620 (22)	9.2
C(9)	0.6652 (17)	0.7670 (12)	-0.1787 (23)	10.9
C(10)	0.5977 (19)	0.6761 (19)	-0.3490 (17)	10.6
C(11)	0.4333 (11)	0.6906 (10)	0.0732 (14)	4.1
C(12)	0.3932 (13)	0.7376 (11)	0.0915 (15)	5.7
C(13)	0.3122 (12)	0.7033 (13)	0.0914 (15)	5.3
C(14)	0.2633 (10)	0.6127 (12)	0.0695 (14)	4.6
C(15)	0.3036 (10)	0.5681 (11)	0.0513 (14)	4.6
C(16)	0.1706 (13)	0.5662 (14)	0.0604 (19)	7.9
(II)				
Cu	0.4585 (1)	0.0	0.5	5.6
O(1)	0.4453 (2)	-0.0388 (3)	0.6479 (7)	6.9
O(2)	0.4955 (2)	0.0614 (3)	0.5882 (7)	7.2
N	0.3919 (4)	0.0	0.5	5.7
C(1)	0.4737 (1)	-0.0525	0.6895 (14)	6.0
C(2)	0.4562 (1)	-0.0877	0.7948 (15)	8.6
C(3)	0.4730 (1)	-0.0540	0.9010 (20)	23.3
C(4)	0.4040 (5)	-0.1102 (7)	0.8137 (21)	18.0
C(5)	0.5396 (1)	0.0791	0.6125 (14)	5.5
C(6)	0.5650 (1)	0.1301	0.6696 (17)	7.7
C(7)	0.5588 (1)	0.1176	0.8069 (18)	15.5
C(8)	0.5353 (6)	0.1570 (5)	0.6377 (20)	13.9
C(9)	0.3895 (4)	0.0404 (4)	0.4827 (11)	6.4
C(10)	0.3480 (4)	0.0435 (4)	0.4822 (11)	7.5
C(11)	0.3054 (4)	0.0	0.5	7.8
C(12)	0.2563 (5)	0.0	0.5	12.2

Table 2. Geometric parameters (Å, °)

(I)			
Cu··Cu ⁱ	2.657 (3)	Cu—N	2.176 (20)
Cu—O(1)	1.967 (10)	O(1)—C(1)	1.214 (26)
Cu—O(2)	1.979 (11)	O(2)—C(6)	1.249 (26)
Cu—O(3)	2.024 (11)	C(1)—O(4) ⁱ	1.235 (28)
Cu—O(4)	1.916 (11)	C(6)—O(3) ⁱ	1.313 (27)
(II)			
Cu··Cu ⁱⁱ	2.648 (5)	Cu—N	2.125 (13)
Cu—O(1)	1.972 (8)	O(1)—C(1)	1.273 (11)
Cu—O(2)	1.969 (8)	O(2)—C(5)	1.255 (7)
(I)			
N—Cu—O(1)	100.6 (6)	O(2)—Cu—O(4)	173.0 (5)
N—Cu—O(2)	92.3 (6)	O(3)—Cu—O(4)	90.7 (4)
N—Cu—O(3)	96.4 (6)	O(1)—C(1)—O(4) ⁱ	128.4 (16)
N—Cu—O(4)	94.8 (6)	O(2)—C(6)—O(3) ⁱ	127.8 (15)
O(1)—Cu—O(2)	89.9 (4)	Cu—O(1)—C(1)	123.3 (13)
O(1)—Cu—O(3)	163.0 (4)	Cu—O(2)—C(6)	118.6 (14)
O(1)—Cu—O(4)	89.0 (4)	Cu—O(3)—C(6) ⁱ	122.9 (12)
O(2)—Cu—O(3)	88.4 (4)	Cu—O(4)—C(1) ⁱ	121.4 (13)
(II)			
N—Cu—O(1)	95.8 (4)	O(2)—Cu—O(2) ⁱⁱⁱ	168.3 (4)
N—Cu—O(2)	95.9 (4)	O(1)—C(1)—O(1) ⁱⁱ	124.1 (11)
O(1)—Cu—O(2)	92.5 (3)	O(2)—C(5)—O(2) ⁱⁱ	127.1 (8)
O(1)—Cu—O(1) ⁱⁱⁱ	168.5 (4)	Cu—O(1)—C(1)	123.5 (5)
O(1)—Cu—O(2) ⁱⁱⁱ	86.3 (3)	Cu—O(2)—C(5)	122.3 (7)

Symmetry codes: (i) $y, x, -z$; (ii) $1 - x + y, y, z$; (iii) $x - y, -y, 1 - z$.

Compound (I): The density was measured by flotation in a tetrabromoethane-cyclohexane mixture. The specimen was coated with adhesive to prevent efflorescence. Laue group $\bar{3}m1$ and systematic absences, $00l$ for $l \neq 3n$, indicated an enantiomorphic pair of the space groups $P3_121$ (No. 152) and $P3_221$ (No. 154). Assuming the space group to be $P3_121$, the structure was solved based on the Patterson function using *SHELXS86* (Sheldrick, 1986). The benzene molecule could not be located on difference syntheses. The enantiomorphic space group $P3_221$ gave almost the same R factor. The large R value may be due to the disorder of the benzene molecule, which was not taken into account in the refinement. The B_{eq} values for the methyl C atoms (9.2–22.5 Å) are abnormally large, suggesting disorder. The bond lengths and angles involving the $\text{C}(\text{CH}_3)_3$ groups were obtained with low accuracy. The structure was refined using *UNICSIII* (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University.

Compound (II): The density was measured by flotation in a tetrabromoethane-cyclohexane mixture. The intensities of five standard reflections decayed by 20%; this was corrected for. Laue group $\bar{3}m1$ and systematic absences, hkl for $-h+k+l \neq 3n$, indicated the space group $R32$ (No. 155), $R3m$ (No. 160) or $R\bar{3}m$ (No. 166). At first, the structure was solved in $R32$. The positions of the Cu atoms on the twofold axis were obtained by direct methods and those of the other non-H atoms by Fourier syntheses. The R value was reduced to 0.072 by introducing the anisotropic thermal parameters. At this stage of the refinement, crystallographic mirror symmetry of the binuclear complex was expected. The space group was then changed to $R\bar{3}m$ to reduce the number of independent non-H atoms from 26 to 16. The refinement gave the same residual factor $R = 0.072$ with normal bond lengths and reasonable thermal parameters. The benzene molecule could not be located on the difference syntheses. The large R value may be due to the disorder of the benzene molecule. The structure was solved using *SHELXS86* and refined using *UNICSIII* with all calculations being performed on a FACOM M-780/10 computer at Keio University.

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Lists of structure factors, anisotropic thermal parameters, and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55490 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1018]

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FeCl₃ Behavior in Acetonitrile: Structures of [FeCl₂(CH₃CN)₄][FeCl₄] and [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN

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Abstract

The structures of the complexes [FeCl₂(CH₃CN)₄][FeCl₄], tetrakis(acetonitrile)dichloroiron(III) tetrachloroferrate(1-), and [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN, pentakis(acetonitrile)chloroaluminium(III) bis[tetrachloroferrate(1-)] acetonitrile solvate, have been determined from single-crystal X-ray diffraction data. [FeCl₂(CH₃CN)₄][FeCl₄] is built up from [FeCl₂(CH₃CN)₄]⁺ octahedra and [FeCl₄]⁻ tetrahedra whereas [AlCl(CH₃CN)₅][FeCl₄]₂·CH₃CN is composed of [AlCl(CH₃CN)₅]²⁺ octahedra, [FeCl₄]⁻ tetrahedra and uncoordinated CH₃CN molecules.

Comment

Very pure starting fluorides are required for fluoride glasses of high optical performance (France, Carter,