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Dimeric Copper(II) Triphenylacetate Adducts with 4-Picoline

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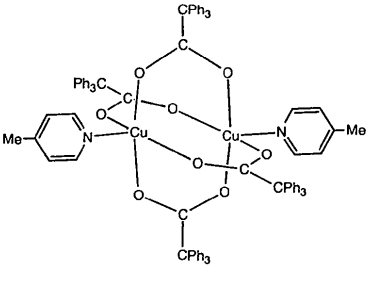
Abstract

The crystal structure of tetrakis(μ-triphenylacetato-*O*:*O'*)-bis[(4-methylpyridine-*N*)copper(II)] ditoluene solvate (I), $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2.2C_7H_8$ (4-pic = 4-picoline), at 120 K, and the analogous $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2.2C_6H_6$ (II) at 290 K were determined by single-crystal X-ray diffraction. The crystal structures of (I) and (II) are essentially identical, and the coordination geometry around the Cu atoms is distorted toward trigonal bipyramidal. The Cu···Cu distances are 2.793 (2) and 2.835 (4) Å in (I) and (II), respectively.

Comment

The electron spin resonance (ESR) spectrum of the title complex, $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$, shows a marked change over the temperature range 133 to 310 K (Jury, 1989). The spectral change can be explained by assuming an interconversion of two conformers of the complex. In order to prove the assumption, X-ray intensity data of a crystal of (II), grown from a benzene solution, were collected at room temperature. The structural determination of (II) was unsuccessful because of the poor experimental resolution. The complex was recrystallized from toluene and intensity measurements of a crystal of (I) were carried out at 120 K. The structure of (I) was solved and as a result of this the structure of (II) could be analyzed with reference to the solved structure of (I). The crystal structures of (I) and (II) are essentially the same except for the accommodation of the solvent molecules (Fig. 1). There is no disorder of the 4-picoline ligands. The crystals did not show X-ray diffraction after efflorescence. In conclusion, the origin of the temperature-dependent ESR spectrum of $[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$ was not resolved by the present studies.



$[Cu(Ph_3CCOO)_2(4\text{-pic})]_2$

The coordination geometry around the Cu atoms is distorted trigonal bipyramidal (TBP) (Fig. 2). The TBP structure of the dimeric copper(II) carboxylates has been observed for a number of copper(II) trichloroacetates (Uekusa *et al.*, 1992, and references therein), $[Cu(Ph_3CCOO)_2(py)]_2.C_6H_6$ (III) (Steward *et al.*, 1991) and $[Cu(PhMe_2CCOO)_2$-(2,6-lutidine)$]_2.C_6H_6$ (Fujita *et al.*, 1993). The distortion of the metal coordination sphere in the dimeric systems from square pyramidal (SP) to trigonal bipyrmidal (TBP) decreases the $-2J$ value and there is a good linear correlation between the $-2J$ value and the Cu···Cu distance (Uekusa *et al.*, 1992).

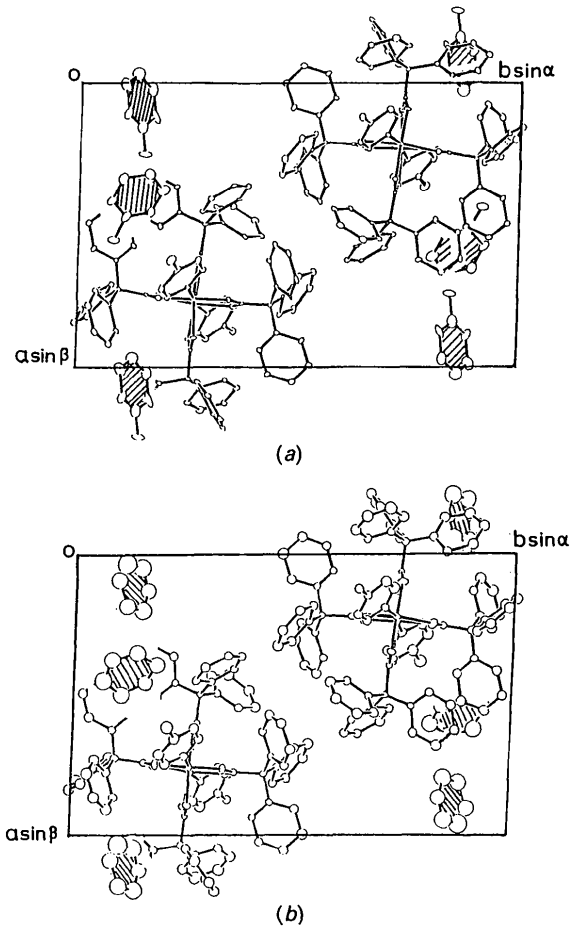


Fig. 1. Projection of the crystal structures along **c** for (*a*) (I) and (*b*) (II). The solvent molecules are shaded for clarity.

Although structural data of the SP type of the copper(II) triphenylacetates are not available at present, the Cu···Cu distance is expected to be *ca* 2.70 Å from considering those of $[Cu(Ph_2MeCCOO)_2(quinoline)]_2.2(quinoline)$, 2.696 (1) Å, and $[Cu(PhMe_2CCOO)_2(quinoline)]_2$, 2.683 (1) Å (Uekusa *et al.*, 1990). Combining the $-2J$ value of the SP type of modification of $[Cu(Ph_3CCOO)_2(py)]_2$ (321 cm^{-1}; Steward *et al.*, 1991), and utilizing the Cu···Cu distance and the $-2J$ value of (III), the $-2J$ values of (I) and (II) are estimated at *ca* 280 cm^{-1}. However, the $-2J$ value was determined to be 326 cm^{-1} by using the efflorescent sample. This observation suggests that the metal coordination of the title complex is converted from TBP to SP when the solvent molecules are lost under the reduced-pressure condition under which the magnetic susceptibility measurement is made. The $-2J$ values of (III) before and after evaporation of the benzene of solvation, are 187 and 173 cm^{-1}, respectively, indicating that the dimeric complex retains the TBP structure. On the other hand, (I) and (II) revert to the SP structure when the solvent of crystallization is removed. The Cu···Cu—N angles in (I) and (II) are in the range 159.8 (2)–166.6 (2)°, whereas the mean Cu···Cu—N angle in (III) is 145.4 (9)°. The deviation of the Cu···Cu—N angle from 180° may be the result of the efficient packing in the crystal (Steward *et al.*, 1991). Therefore, it seems that (III) is frozen in the TBP structure due to a larger energy barrier to overcome in order to revert to the SP form.

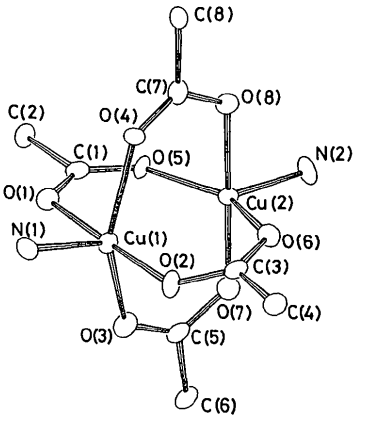


Fig. 2. *ORTEP* drawing (Johnson, 1965) of the central cage structure of the binuclear complex in (I) with thermal ellipsoids scaled at the 50% probability level.

Experimental

Compound (I)

Crystal data

$[Cu_2(C_{20}H_{15}O_2)_4(C_6H_7N)_2].2C_7H_8$
M_r = 1647.0
Triclinic
$P\bar{1}$
a = 15.595 (3) Å
b = 24.390 (5) Å
c = 11.868 (4) Å
α = 104.07 (2)°
β = 74.05 (2)°
γ = 95.35 (1)°
V = 4208 (2) Å^3
Z = 2
D_x = 1.30 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 50 reflections
θ = 10–15°
μ = 0.56 mm^{-1}
T = 120 K
Plate
0.45 × 0.40 × 0.05 mm
Green

Data collection

Rigaku AFC-5 diffractometer
θ-2θ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.786, T_{max} = 0.970
15 561 measured reflections
14 719 independent reflections
8774 observed reflections [$F > 3\sigma(F)$]
R_{int} = 0.018
θ_{max} = 25.0°
h = −18 → 18
k = −28 → 28
l = 0 → 14
5 standard reflections monitored every 100 reflections
intensity variation: 4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.35
Final R = 0.078	$\Delta\rho_{max}$ = 1.05 e Å^{-3}
wR = 0.079	$\Delta\rho_{min}$ = −0.68 e Å^{-3}
S = 2.20	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
8774 reflections	
1063 parameters	
$w = [\sigma^2(F) + (0.015F)^2]^{-1}$	

Compound (II)

Crystal data

$[Cu_2(C_{20}H_{15}O_2)_4(C_6H_7N)_2]\cdot 2C_6H_6$	D_x = 1.25 Mg m^{-3}
M_r = 1618.9	D_m = 1.25 (1) Mg m^{-3}
Triclinic	Mo $K\alpha$ radiation
$P\bar{1}$	λ = 0.71073 Å
a = 15.569 (2) Å	Cell parameters from 40 reflections
b = 24.619 (4) Å	θ = 10–15°
c = 12.005 (3) Å	μ = 0.55 mm^{-1}
α = 103.75 (2)°	T = 290 K
β = 73.62 (1)°	Plate
γ = 95.94 (1)°	0.35 × 0.15 × 0.15 mm
V = 4285 (1) Å^3	Green
Z = 2	

Data collection

Rigaku AFC-5 diffractometer	3258 observed reflections $[F > 3\sigma(F)]$
θ–2θ scans	R_{int} = 0.021
Absorption correction: by integration from crystal shape	θ_{max} = 20.0°
T_{min} = 0.893, T_{max} = 0.937	$h = -14 \rightarrow 14$
8500 measured reflections	$k = -23 \rightarrow 23$
7906 independent reflections	$l = 0 \rightarrow 11$
	4 standard reflections monitored every 100 reflections
	intensity variation: 3%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.06
Final R = 0.091	$\Delta\rho_{max}$ = 0.62 e Å^{-3}
wR = 0.079	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
S = 1.99	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
3258 reflections	
515 parameters	
$w = [\sigma^2(F) + (0.015F)^2]^{-1}$	

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

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Compound (I)				
Cu(1)	0.21867 (6)	0.73039 (4)	0.97034 (9)	1.2
Cu(2)	0.23617 (6)	0.73237 (4)	0.73070 (9)	1.1
O(1)	0.3436 (3)	0.7189 (2)	0.9400 (4)	1.4
O(2)	0.0952 (3)	0.7423 (2)	0.9916 (4)	1.6
O(3)	0.2464 (3)	0.8149 (2)	0.9756 (5)	1.7
O(4)	0.2101 (3)	0.6446 (2)	0.8640 (4)	1.3
O(5)	0.3653 (3)	0.7261 (2)	0.7498 (4)	1.3
O(6)	0.0999 (3)	0.7305 (2)	0.7978 (4)	1.5
O(7)	0.2394 (3)	0.8123 (2)	0.7893 (4)	1.7
O(8)	0.2326 (3)	0.6521 (2)	0.6746 (4)	1.4
N(1)	0.1859 (4)	0.7009 (3)	1.1292 (5)	1.3
N(2)	0.2748 (4)	0.7464 (3)	0.5563 (5)	1.6
C(1)	0.3916 (4)	0.7192 (3)	0.8356 (7)	1.2
C(2)	0.4938 (4)	0.7102 (3)	0.8169 (7)	1.4
C(3)	0.0595 (5)	0.7365 (3)	0.9052 (7)	1.3
C(4)	−0.0451 (4)	0.7414 (3)	0.9477 (7)	1.3
C(5)	0.2488 (4)	0.8381 (3)	0.8925 (7)	1.5
C(6)	0.2690 (5)	0.9030 (3)	0.9059 (7)	1.5
C(7)	0.2202 (4)	0.6236 (3)	0.7554 (7)	1.3
C(8)	0.2147 (5)	0.5581 (3)	0.7092 (7)	1.3
C(9)	0.5383 (5)	0.7690 (3)	0.8564 (7)	1.5
C(10)	0.6299 (5)	0.7770 (3)	0.8054 (8)	2.1
C(11)	0.6728 (5)	0.8293 (4)	0.8454 (8)	2.4
C(12)	0.6248 (5)	0.8719 (3)	0.9337 (8)	2.7
C(13)	0.5324 (5)	0.8635 (3)	0.9858 (8)	2.3
C(14)	0.4893 (5)	0.8123 (3)	0.9458 (7)	1.9
C(15)	0.5012 (4)	0.6714 (3)	0.8985 (7)	1.4
C(16)	0.4507 (5)	0.6194 (3)	0.8925 (7)	1.9
C(17)	0.4535 (5)	0.5830 (4)	0.9659 (8)	2.3
C(18)	0.5090 (5)	0.5975 (4)	1.0452 (8)	2.7
C(19)	0.5594 (6)	0.6488 (4)	1.0521 (8)	2.9
C(20)	0.5556 (5)	0.6859 (3)	0.9797 (7)	2.0
C(21)	0.5389 (4)	0.6846 (3)	0.6836 (7)	1.4
C(22)	0.5833 (4)	0.6340 (3)	0.6460 (7)	1.6
C(23)	0.6308 (5)	0.6151 (3)	0.5219 (7)	2.1
C(24)	0.6335 (5)	0.6467 (3)	0.4389 (7)	1.8
C(25)	0.5869 (5)	0.6984 (4)	0.4770 (8)	2.3
C(26)	0.5401 (5)	0.7170 (3)	0.5979 (7)	1.7
C(27)	−0.0765 (4)	0.7123 (3)	1.0560 (7)	1.4
C(28)	−0.0508 (5)	0.6577 (3)	1.0393 (7)	1.8
C(29)	−0.0783 (5)	0.6295 (4)	1.1333 (8)	2.4
C(30)	−0.1319 (5)	0.6566 (4)	1.2486 (8)	2.8
C(31)	−0.1563 (6)	0.7120 (4)	1.2639 (8)	3.1
C(32)	−0.1302 (5)	0.7410 (4)	1.1679 (7)	2.3
C(33)	−0.0918 (4)	0.7122 (3)	0.8484 (7)	1.4
C(34)	−0.1735 (5)	0.6822 (3)	0.8809 (8)	2.0
C(35)	−0.2205 (5)	0.6581 (4)	0.7933 (8)	2.7
C(36)	−0.1874 (5)	0.6643 (4)	0.6739 (8)	2.7
C(37)	−0.1069 (5)	0.6951 (4)	0.6416 (8)	2.4
C(38)	−0.0595 (5)	0.7196 (3)	0.7298 (7)	2.0
C(39)	−0.0626 (5)	0.8063 (3)	0.9856 (7)	1.6
C(40)	−0.0220 (5)	0.8412 (3)	1.0692 (7)	1.8
C(41)	−0.0386 (5)	0.8991 (3)	1.1057 (8)	2.3
C(42)	−0.0957 (5)	0.9233 (4)	1.0602 (8)	2.5
C(43)	−0.1362 (5)	0.8873 (4)	0.9744 (8)	2.7
C(44)	−0.1207 (5)	0.8292 (3)	0.9388 (8)	2.2
C(45)	0.2185 (5)	0.9239 (3)	0.8286 (7)	1.6
C(46)	0.2612 (6)	0.9560 (3)	0.7459 (7)	2.4
C(47)	0.2136 (6)	0.9729 (4)	0.6739 (8)	3.1
C(48)	0.1236 (6)	0.9571 (4)	0.6854 (8)	2.8
C(49)	0.0803 (6)	0.9243 (4)	0.7688 (8)	2.7
C(50)	0.1265 (5)	0.9072 (3)	0.8396 (7)	2.1
C(51)	0.2419 (5)	0.9337 (3)	1.0392 (7)	1.6
C(52)	0.1779 (5)	0.9759 (3)	1.0842 (8)	2.4
C(53)	0.1577 (5)	1.0042 (4)	1.2062 (8)	3.0
C(54)	0.2011 (6)	0.9904 (4)	1.2850 (8)	2.7
C(55)	0.2655 (5)	0.9472 (3)	1.2396 (8)	2.5
C(56)	0.2854 (5)	0.9201 (3)	1.1187 (7)	2.0
C(57)	0.3706 (5)	0.9113 (3)	0.8532 (7)	1.6
C(58)	0.4201 (5)	0.8714 (3)	0.7578 (7)	1.8
C(59)	0.5114 (5)	0.8833 (3)	0.7060 (8)	2.4
C(60)	0.5508 (5)	0.9341 (4)	0.7461 (8)	2.7
C(61)	0.5015 (5)	0.9750 (4)	0.8439 (8)	2.8
C(62)	0.4116 (5)	0.9632 (3)	0.8966 (8)	2.6
C(63)	0.1169 (5)	0.5413 (3)	0.7093 (7)	1.4
C(64)	0.0572 (5)	0.5796 (3)	0.7030 (7)	1.4
C(65)	−0.0300 (5)	0.5612 (3)	0.6956 (7)	1.7
C(66)	−0.0574 (5)	0.5046 (4)	0.6934 (7)	2.1
C(67)	0.0028 (5)	0.4658 (4)	0.7002 (7)	2.1
C(68)	0.0895 (5)	0.4840 (3)	0.7074 (7)	1.8
C(69)	0.2757 (5)	0.5428 (3)	0.5791 (7)	1.3

C(70)	0.3653 (5)	0.5626 (3)	0.5578 (7)	1.9
C(71)	0.4224 (5)	0.5492 (3)	0.4420 (8)	2.4
C(72)	0.3926 (5)	0.5185 (3)	0.3445 (8)	2.4
C(73)	0.3018 (5)	0.4988 (3)	0.3657 (8)	2.2
C(74)	0.2440 (5)	0.5112 (3)	0.4833 (7)	1.5
C(75)	0.2399 (5)	0.5289 (3)	0.7961 (7)	1.2
C(76)	0.3123 (5)	0.4918 (3)	0.7563 (8)	2.0
C(77)	0.3281 (5)	0.4614 (3)	0.8378 (8)	2.5
C(78)	0.2738 (6)	0.4679 (4)	0.9543 (8)	2.9
C(79)	0.2000 (6)	0.5048 (3)	0.9935 (8)	2.4
C(80)	0.1854 (5)	0.5349 (3)	0.9128 (7)	2.0
C(81)	0.2338 (5)	0.6591 (3)	1.1371 (7)	2.1
C(82)	0.2142 (5)	0.6374 (3)	1.2412 (7)	2.0
C(83)	0.1459 (5)	0.6609 (3)	1.3422 (7)	1.8
C(84)	0.0966 (5)	0.7041 (4)	1.3306 (7)	2.3
C(85)	0.1176 (5)	0.7221 (4)	1.2230 (7)	2.1
C(86)	0.1247 (6)	0.6409 (4)	1.4593 (7)	2.2
C(87)	0.3349 (5)	0.7139 (3)	0.4681 (7)	2.1
C(88)	0.3671 (6)	0.7253 (4)	0.3540 (8)	2.6
C(89)	0.3345 (6)	0.7711 (4)	0.3289 (7)	2.6
C(90)	0.2709 (6)	0.8052 (3)	0.4200 (7)	2.4
C(91)	0.2425 (5)	0.7918 (3)	0.5339 (7)	2.0
C(92)	0.3694 (6)	0.7860 (4)	0.2051 (8)	3.6
C(101)	0.4772 (7)	0.1098 (5)	0.6225 (11)	5.7
C(102)	0.4614 (7)	0.1657 (4)	0.6351 (10)	4.3
C(103)	0.4183 (7)	0.0761 (5)	0.6980 (10)	4.8
C(104)	0.3411 (8)	0.1010 (5)	0.7818 (11)	6.1
C(105)	0.3250 (7)	0.1614 (5)	0.7969 (10)	5.2
C(106)	0.3835 (8)	0.1926 (6)	0.7286 (11)	6.3
C(107)	0.5580 (7)	0.0811 (5)	0.5375 (10)	5.7
C(108)	0.1591 (9)	0.1432 (5)	0.5056 (12)	7.9
C(109)	0.1222 (9)	0.1717 (5)	0.4429 (11)	6.4
C(110)	0.0259 (9)	0.1643 (5)	0.4604 (11)	7.0
C(111)	−0.0286 (10)	0.1315 (6)	0.5402 (14)	9.0
C(112)	0.0092 (9)	0.1037 (6)	0.6004 (11)	7.3
C(113)	0.1098 (8)	0.1100 (5)	0.5847 (10)	5.8
C(114)	0.2539 (7)	0.1506 (6)	0.4905 (13)	8.6

Compound (II)

Cu(1)	0.2253 (2)	0.7302 (1)	0.9645 (2)	2.9
Cu(2)	0.2437 (2)	0.7315 (1)	0.7234 (2)	3.0
O(1)	0.3482 (7)	0.7210 (5)	0.9385 (9)	3.2
O(2)	0.1033 (7)	0.7409 (5)	0.9866 (10)	4.0
O(3)	0.2520 (8)	0.8137 (5)	0.9649 (10)	4.3
O(4)	0.2173 (7)	0.6460 (5)	0.8584 (9)	3.2
O(5)	0.3734 (7)	0.7240 (5)	0.7463 (9)	3.4
O(6)	0.1072 (7)	0.7339 (5)	0.7965 (9)	3.5
O(7)	0.2521 (8)	0.8115 (4)	0.7788 (11)	4.1
O(8)	0.2356 (7)	0.6532 (4)	0.6697 (9)	3.4
N(1)	0.1919 (9)	0.7032 (6)	1.1219 (12)	3.5
N(2)	0.2829 (9)	0.7445 (6)	0.5512 (13)	4.3
C(1)	0.3982 (11)	0.7175 (7)	0.8325 (14)	2.5
C(2)	0.5011 (10)	0.7113 (6)	0.8144 (14)	2.0
C(3)	0.0671 (10)	0.7378 (6)	0.9025 (14)	2.0
C(4)	−0.0374 (11)	0.7441 (7)	0.9444 (15)	3.3
C(5)	0.2586 (11)	0.8369 (7)	0.8835 (15)	2.8
C(6)	0.2761 (11)	0.9025 (7)	0.8905 (15)	3.5
C(7)	0.2241 (11)	0.6264 (7)	0.7521 (15)	2.7
C(8)	0.2195 (10)	0.5593 (7)	0.7052 (14)	2.6
C(9)	0.5427 (11)	0.7706 (7)	0.8562 (15)	2.8
C(10)	0.6377 (12)	0.7766 (8)	0.8034 (17)	4.6
C(11)	0.6816 (14)	0.8307 (9)	0.8459 (19)	6.2
C(12)	0.6282 (12)	0.8708 (8)	0.9324 (17)	4.8
C(13)	0.5397 (13)	0.8610 (8)	0.9818 (17)	5.3
C(14)	0.4943 (11)	0.8116 (7)	0.9439 (16)	3.7
C(15)	0.5058 (11)	0.6723 (7)	0.8977 (15)	3.5
C(16)	0.4537 (11)	0.6205 (7)	0.8899 (16)	3.9
C(17)	0.4562 (13)	0.5834 (8)	0.9651 (18)	5.8
C(18)	0.5147 (13)	0.5982 (9)	1.0367 (19)	6.1
C(19)	0.5693 (14)	0.6465 (9)	1.0448 (19)	6.6
C(20)	0.5662 (13)	0.6861 (8)	0.9749 (18)	5.3
C(21)	0.5450 (11)	0.6858 (7)	0.6821 (15)	3.2
C(22)	0.5909 (11)	0.6334 (7)	0.6459 (15)	3.3
C(23)	0.6371 (12)	0.6183 (7)	0.5235 (16)	4.1
C(24)	0.6394 (12)	0.6484 (7)	0.4401 (16)	4.1
C(25)	0.5964 (13)	0.7011 (8)	0.4801 (17)	5.2
C(26)	0.5502 (12)	0.7214 (8)	0.6011 (16)	4.1
C(27)	−0.0728 (11)	0.7102 (7)	1.0457 (16)	3.6
C(28)	−0.0489 (12)	0.6565 (8)	1.0317 (16)	4.3
C(29)	−0.0790 (14)	0.6279 (9)	1.1209 (19)	6.2
C(30)	−0.1275 (15)	0.6543 (9)	1.2297 (20)	7.6
C(31)	−0.1565 (15)	0.7081 (10)	1.2527 (21)	8.1
C(32)	−0.1245 (13)	0.7380 (8)	1.1556 (18)	6.0
C(33)	−0.0817 (11)	0.7179 (7)	0.8419 (16)	3.7
C(34)	−0.1623 (12)	0.6841 (7)	0.8727 (16)	4.4
C(35)	−0.2062 (13)	0.6627 (8)	0.7799 (18)	6.0
C(36)	−0.1740 (13)	0.6744 (8)	0.6731 (18)	6.0
C(37)	−0.0955 (14)	0.7106 (9)	0.6452 (19)	7.0
C(38)	−0.0499 (13)	0.7318 (8)	0.7344 (17)	5.0
C(39)	−0.0541 (12)	0.8081 (7)	0.9900 (16)	4.0
C(40)	−0.0039 (12)	0.8398 (8)	1.0625 (16)	4.3
C(41)	−0.0275 (13)	0.8987 (8)	1.1052 (18)	5.5
C(42)	−0.0908 (13)	0.9225 (8)	1.0755 (18)	6.1
C(43)	−0.1359 (14)	0.8890 (9)	1.0030 (19)	6.5
C(44)	−0.1237 (13)	0.8314 (8)	0.9620 (18)	5.6
C(45)	0.2248 (12)	0.9199 (7)	0.8121 (16)	4.1
C(46)	0.2700 (13)	0.9480 (8)	0.7280 (18)	6.0
C(47)	0.2209 (14)	0.9636 (9)	0.6520 (20)	7.3
C(48)	0.1359 (14)	0.9466 (9)	0.6659 (19)	6.7
C(49)	0.0923 (14)	0.9177 (9)	0.7492 (19)	6.5
C(50)	0.1361 (12)	0.9031 (7)	0.8237 (16)	3.9
C(51)	0.2415 (12)	0.9321 (7)	1.0264 (16)	4.1
C(52)	0.1853 (13)	0.9777 (8)	1.0584 (18)	6.0
C(53)	0.1637 (13)	1.0042 (8)	1.1846 (18)	6.0
C(54)	0.1968 (14)	0.9874 (9)	1.2614 (19)	6.7
C(55)	0.2543 (13)	0.9455 (8)	1.2311 (18)	5.9
C(56)	0.2805 (13)	0.9160 (8)	1.1061 (18)	5.6
C(57)	0.3766 (11)	0.9107 (7)	0.8421 (15)	3.3
C(58)	0.4296 (12)	0.8727 (8)	0.7529 (17)	4.7
C(59)	0.5254 (13)	0.8844 (8)	0.7054 (18)	6.0
C(60)	0.5608 (13)	0.9376 (8)	0.7502 (18)	5.8
C(61)	0.5073 (13)	0.9778 (8)	0.8397 (17)	5.0
C(62)	0.4215 (13)	0.9632 (8)	0.8882 (17)	5.2
C(63)	0.1166 (11)	0.5448 (7)	0.7068 (15)	2.9
C(64)	0.0621 (11)	0.5815 (7)	0.6964 (15)	2.9
C(65)	−0.0256 (11)	0.5638 (7)	0.6916 (16)	3.8
C(66)	−0.0565 (13)	0.5078 (8)	0.6948 (17)	5.1
C(67)	0.0012 (14)	0.4670 (9)	0.7002 (19)	6.3
C(68)	0.0918 (12)	0.4868 (8)	0.7145 (17)	4.6
C(69)	0.2812 (11)	0.5448 (7)	0.5771 (15)	2.7
C(70)	0.3690 (11)	0.5654 (7)	0.5594 (16)	3.4
C(71)	0.4262 (13)	0.5510 (8)	0.4442 (18)	5.3
C(72)	0.3965 (13)	0.5239 (8)	0.3487 (17)	5.1
C(73)	0.3056 (13)	0.5018 (8)	0.3674 (18)	5.5
C(74)	0.2462 (12)	0.5126 (7)	0.4834 (16)	3.9
C(75)	0.2413 (11)	0.5309 (7)	0.7970 (15)	2.9
C(76)	0.3112 (12)	0.4931 (8)	0.7534 (17)	4.8
C(77)	0.3268 (13)	0.4624 (8)	0.8317 (18)	5.8
C(78)	0.2739 (12)	0.4724 (8)	0.9493 (17)	5.2
C(79)	0.2026 (12)	0.5091 (8)	0.9906 (17)	4.8
C(80)	0.1845 (12)	0.5385 (7)	0.9104 (16)	4.0
C(81)	0.2390 (12)	0.6623 (8)	1.1315 (17)	5.3
C(82)	0.2175 (12)	0.6409 (8)	1.2395 (17)	4.6
C(83)	0.1495 (12)	0.6620 (8)	1.3328 (16)	4.2
C(84)	0.1008 (13)	0.7029 (8)	1.3226 (19)	6.3
C(85)	0.1228 (14)	0.7218 (9)	1.2145 (19)	6.8
C(86)	0.1264 (12)	0.6404 (7)	1.4515 (16)	4.2
C(87)	0.3448 (12)	0.7113 (8)	0.4663 (17)	4.9
C(88)	0.3800 (13)	0.7240 (8)	0.3475 (18)	5.8
C(89)	0.3453 (14)	0.7696 (9)	0.3306 (19)	6.7
C(90)	0.2881 (14)	0.8035 (9)	0.4137 (19)	6.6
C(91)	0.2532 (13)	0.7893 (8)	0.5282 (18)	5.8
C(92)	0.3842 (15)	0.7880 (10)	0.2035 (21)	8.3
C(101)	0.5500 (22)	0.9328 (14)	1.3474 (29)	16.2
C(102)	0.6255 (21)	0.9142 (13)	1.2648 (28)	14.5
C(103)	0.6481 (21)	0.8585 (13)	1.2284 (28)	14.5
C(104)	0.6060 (20)	0.8147 (13)	1.2970 (27)	14.4
C(105)	0.5421 (18)	0.8391 (12)	1.3974 (25)	11.8
C(106)	0.5006 (20)	0.8918 (13)	1.4242 (27)	14.4
C(111)	0.1853 (21)	0.1157 (13)	0.5684 (29)	14.9
C(112)	0.2018 (22)	0.1507 (14)	0.4843 (30)	16.4
C(113)	0.1312 (19)	0.1606 (12)	0.4399 (26)	12.7
C(114)	0.0498 (23)	0.1462 (15)	0.4770 (31)	17.2
C(115)	0.0352 (26)	0.1123 (16)	0.5564 (34)	20.2
C(116)	0.0925 (21)	0.0956 (13)	0.5844 (28)	14.5

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

	(I)	(II)
Cu(1)—Cu(2)	2.793 (2)	2.835 (4)
Cu(1)—O(1)	1.916 (5)	1.879 (12)
Cu(1)—O(2)	1.912 (5)	1.880 (12)
Cu(1)—O(3)	2.056 (5)	2.054 (13)
Cu(1)—O(4)	2.178 (5)	2.173 (11)
Cu(1)—N(1)	2.096 (7)	2.066 (16)
Cu(2)—O(5)	2.111 (5)	2.145 (12)
Cu(2)—O(6)	2.055 (4)	2.059 (10)
Cu(2)—O(7)	1.905 (5)	1.927 (10)
Cu(2)—O(8)	1.909 (5)	1.885 (10)
Cu(2)—N(2)	2.094 (6)	2.083 (16)
Cu(2)—Cu(1)—O(1)	92.1 (1)	93.2 (4)
Cu(2)—Cu(1)—O(2)	84.7 (2)	85.2 (4)
Cu(2)—Cu(1)—O(3)	79.2 (1)	78.3 (4)
Cu(2)—Cu(1)—O(4)	70.0 (1)	68.8 (3)
Cu(2)—Cu(1)—N(1)	159.8 (2)	160.5 (5)
Cu(1)—Cu(2)—O(5)	72.5 (1)	71.0 (3)
Cu(1)—Cu(2)—O(6)	78.4 (1)	77.1 (3)
Cu(1)—Cu(2)—O(7)	83.9 (1)	83.8 (3)
Cu(1)—Cu(2)—O(8)	95.2 (1)	96.0 (3)
Cu(1)—Cu(2)—N(2)	166.6 (2)	166.5 (4)
O(1)—Cu(1)—O(2)	176.8 (2)	178.0 (5)
O(3)—Cu(1)—O(4)	148.7 (2)	146.7 (5)
O(3)—Cu(1)—N(1)	120.3 (2)	120.4 (6)
O(4)—Cu(1)—N(1)	90.9 (2)	92.9 (6)
O(5)—Cu(2)—O(6)	150.5 (2)	148.0 (4)
O(7)—Cu(2)—O(8)	179.1 (2)	179.8 (4)
O(5)—Cu(2)—N(2)	97.4 (2)	99.0 (5)
O(6)—Cu(2)—N(2)	112.2 (2)	113.0 (5)
Cu(1)—O(1)—C(1)	117.1 (5)	117.4 (10)
Cu(1)—O(2)—C(3)	123.7 (5)	124.6 (10)
Cu(1)—O(3)—C(5)	124.9 (5)	127.9 (12)
Cu(1)—O(4)—C(7)	134.3 (5)	134.6 (10)
Cu(2)—O(5)—C(1)	131.8 (5)	132.3 (10)
Cu(2)—O(6)—C(3)	125.6 (5)	126.7 (10)
Cu(2)—O(7)—C(5)	125.6 (5)	125.0 (12)
Cu(2)—O(8)—C(7)	115.7 (5)	113.9 (11)

Compound (I): $[Cu(Ph_3CCOO)_2(H_2O)]_2$ (Steward *et al.*, 1986) (1.0 g, 1.5 mmol) was dissolved in benzene (40 ml). On dropwise addition of 4-picoline (0.14 g, 1.5 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 (30:70 *v/v*) and air dried. A crystal grown from toluene solution was coated with adhesive and cooled in a cold N_2 stream. The structure was solved by the Patterson-Fourier method. All non-H atoms were refined with anisotropic thermal parameters. *Compound* (II): Crystals were grown from a benzene solution. The density was measured by flotation in a tetrachloromethane-cyclohexane mixture. The crystal was coated with adhesive to prevent efflorescence. The atomic coordinates of (I) were utilized as initial parameters. The C and N atoms were refined isotropically to reduce the number of parameters.

Both structures were refined using *UNICS*III (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University. The relatively large *R* values [0.078 for (I) and 0.091 for (II)] may arise partly from the orientational disorder of the solvent molecules.

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 71058 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1031]

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Chloro(trimesitylphosphine)gold(I)

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Abstract

Chloro(trimesitylphosphine)gold(I), $[AuCl(C_9H_{11})P_3]$, has approximate threefold symmetry in the solid state [dihedral angles between the mesityl ring planes and the relevant Au—P—C planes are 47.0 (1), 48.0 (1) and 48.5 (1)°]. The Au atom has a linear coordination geometry with Au—Cl and Au—P bond lengths of 2.2716 (19) and 2.2634 (15) Å, respectively, and a P—Au—Cl bond angle of 178.01 (8)°. The C_{ar}—C_{ar} bond lengths are in the range 1.360 (10) to 1.424 (8) Å, while the range of C_{ar}—C_{sp^3} distances lies between 1.499 (10) and 1.529 (9) Å.

Comment

The structural chemistry of monophosphine gold(I) halides continues to attract considerable attention and