

I(1)—Ir(1)—P(1)	92.50 (3)	C(2)—P(2)—C(19)	105.1 (2)
I(1)—Ir(1)—P(2)	92.62 (3)	C(2)—P(2)—C(25)	107.4 (2)
I(1)—Ir(1)—N(1)	86.77 (10)	C(19)—P(2)—C(25)	98.9 (2)
P(1)—Ir(1)—P(2)	174.46 (4)	N(1)—Si(1)—C(1)	104.5 (2)
P(1)—Ir(1)—N(1)	89.3 (1)	N(1)—Si(1)—C(3)	110.3 (2)
P(2)—Ir(1)—N(1)	88.9 (1)	N(1)—Si(1)—C(4)	111.1 (2)
I(1)—Ir(1)—H(1)	176 (1)	C(1)—Si(1)—C(3)	111.4 (2)
I(1)—Ir(1)—H(2)	88 (1)	C(1)—Si(1)—C(4)	109.4 (2)
P(1)—Ir(1)—H(1)	87 (1)	C(3)—Si(1)—C(4)	110.0 (3)
P(1)—Ir(1)—H(2)	90 (1)	N(1)—Si(2)—C(2)	103.9 (2)
P(2)—Ir(1)—H(1)	87 (1)	N(1)—Si(2)—C(5)	112.2 (2)
P(2)—Ir(1)—H(2)	91 (1)	N(1)—Si(2)—C(6)	110.4 (2)
N(1)—Ir(1)—H(1)	90 (1)	C(2)—Si(2)—C(5)	109.7 (2)
N(1)—Ir(1)—H(2)	174 (1)	C(2)—Si(2)—C(6)	110.3 (3)
H(1)—Ir(1)—H(2)	95 (2)	C(5)—Si(2)—C(6)	110.3 (3)
Ir(1)—P(1)—C(1)	106.6 (1)	Ir(1)—N(1)—Si(1)	108.7 (2)
Ir(1)—P(1)—C(7)	120.6 (2)	Ir(1)—N(1)—Si(2)	108.5 (2)
Ir(1)—P(1)—C(13)	116.2 (2)	Si(1)—N(1)—Si(2)	125.0 (2)
C(1)—P(1)—C(7)	106.3 (2)	Ir(1)—N(1)—H(3)	87 (3)
C(1)—P(1)—C(13)	105.6 (2)	Si(1)—N(1)—H(3)	113 (3)
C(7)—P(1)—C(13)	100.2 (2)	Si(2)—N(1)—H(3)	107 (3)
Ir(1)—P(2)—C(2)	107.5 (2)	P(1)—C(1)—Si(1)	107.4 (2)
Ir(1)—P(2)—C(19)	121.4 (2)	P(2)—C(2)—Si(2)	109.3 (2)
Ir(1)—P(2)—C(25)	115.4 (2)		

The metal hydride and amine H atoms were refined with isotropic displacement parameters. The remaining H atoms were fixed in calculated positions (methyl groups staggered, with C—H = 0.98 Å and displacement parameters 20% larger than those of the parent atoms).

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, torsion angles and selected non-bonded contacts < 3.80 Å, have been deposited with the IUCr (Reference: FG1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorotris(triphenylphosphine)copper(I) Tetrahydrofuran Solvate

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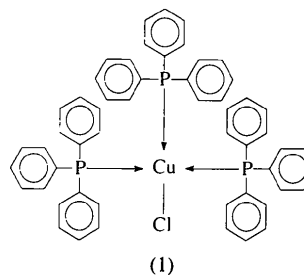
(Received 28 April 1995; accepted 14 September 1995)

Abstract

The structure of [CuCl{P(C₆H₅)₃}₃].C₄H₈O consists of discrete [CuCl{P(C₆H₅)₃}₃] molecules containing pseudo-tetrahedrally coordinated copper, together with one disordered tetrahydrofuran solvent molecule per molecule of complex.

Comment

The structure of [CuCl{P(C₆H₅)₃}₃], (1), has been determined previously in its unsolvated form [(2); Gill *et al.*, 1976], as a 1:3 solvate with tetrahydrofuran [(3); Foltg, Huffman, Mahoney, Stryker & Caulton, 1987] and as a 1:1 acetone solvate [(4); Barron *et al.*, 1987].



One of these previously determined structures, (2), exhibits very nearly tetrahedral coordination geometry [angles 108.41 (7)–110.51 (6)°], with the Cu—Cl distances [mean 2.335 (2) Å] shorter than the Cu—P distances [mean 2.351 (1) Å]. In structures (3) and (4), the Cu—P distances are shorter than the Cu—Cl distances [2.3183 (17) and 2.3469 (27) Å, respectively, for (3); 2.326 (4) and 2.349 (6) Å for (4)] and a concomitant increase of the P—Cu—P angles [115.00 (4) and 115.0 (2)°, respectively, for (3) and (4)] relative to those in (2) is exhibited. This may be considered to be a consequence of the increased mutual steric repulsion of the triphenylphosphine ligands in (3) and (4) relative to (2). However, in the structure described herein, (1), the Cu—Cl bond length [2.324 (2) Å] is shorter than the Cu—P

bond lengths [mean 2.346 (1) Å], as is the case of (2), yet interligand angles corresponding closely to those of (3) and (4) are retained. This is in accordance with the observation that the presence of solvent of crystallization has a strong effect on the coordination geometry of [CuX{P(C₆H₅)₃}₃] (X = Cl, Br, I) complexes (Barron *et al.*, 1987).

Absorption correction: $h = 0 \rightarrow 12$
 ψ scans (SHELXTL; $k = 0 \rightarrow 9$
 Sheldrick, 1986) $l = -35 \rightarrow 35$
 $T_{\min} = 0.864$, $T_{\max} = 0.881$ 3 standard reflections monitored every 97 reflections
 5305 measured reflections
 5087 independent reflections intensity decay: 1%
 2832 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} = 0.002$
 $R(F) = 0.0609$ $\Delta\rho_{\max} = 0.300 \text{ e } \text{Å}^{-3}$
 $wR(F^2) = 0.1372$ $\Delta\rho_{\min} = -0.336 \text{ e } \text{Å}^{-3}$
 $S = 0.945$ Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 5086 reflections
 584 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.0379P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

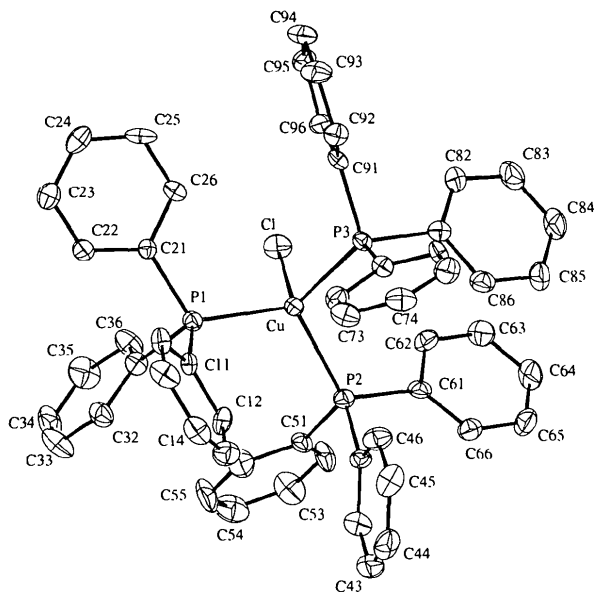


Fig. 1. The structure of the title complex with 40% probability ellipsoids and partial labelling scheme. H atoms have been omitted for clarity.

Experimental

Crystals of the title compound were obtained from tetrahydrofuran solution.

Crystal data

[CuCl(C₁₈H₁₅P)₃].C₄H₈O

$M_r = 957.90$

Monoclinic

$P2_1/c$

$a = 13.314 (5) \text{ Å}$

$b = 10.077 (5) \text{ Å}$

$c = 36.510 (10) \text{ Å}$

$\beta = 94.85 (3)^\circ$

$V = 4880 (3) \text{ Å}^3$

$Z = 4$

$D_x = 1.304 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ Å}$

Cell parameters from 25 reflections

$\theta = 7.0\text{--}11.0^\circ$

$\mu = 0.642 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block

$0.20 \times 0.20 \times 0.20 \text{ mm}$

Colourless

Data collection

Siemens R3m diffractometer

$R_{\text{int}} = 0.048$

Wyckoff scans

$\theta_{\text{max}} = 22.52^\circ$

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

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cu	0.30117 (6)	0.71255 (9)	0.10146 (2)	0.0296 (3)
Cl	0.3177 (2)	0.4986 (2)	0.07880 (6)	0.0484 (6)
P1	0.17698 (14)	0.8073 (2)	0.06004 (5)	0.0320 (6)
P2	0.25456 (15)	0.6809 (2)	0.16130 (5)	0.0346 (6)
P3	0.46700 (13)	0.7925 (2)	0.10126 (5)	0.0305 (5)
C11	0.1500 (5)	0.9832 (7)	0.0686 (2)	0.031 (2)
C12	0.1312 (6)	1.0163 (9)	0.1046 (2)	0.047 (2)
C13	0.1173 (6)	1.1467 (10)	0.1142 (2)	0.056 (3)
C14	0.1230 (6)	1.2467 (8)	0.0886 (3)	0.053 (3)
C15	0.1421 (6)	1.2149 (9)	0.0534 (3)	0.056 (2)
C16	0.1561 (5)	1.0841 (8)	0.0436 (2)	0.039 (2)
C21	0.2015 (5)	0.8012 (7)	0.0117 (2)	0.030 (2)
C22	0.1287 (6)	0.8333 (7)	-0.0165 (2)	0.046 (2)
C23	0.1473 (7)	0.8254 (8)	-0.0528 (2)	0.057 (3)
C24	0.2402 (7)	0.7839 (10)	-0.0616 (2)	0.066 (3)
C25	0.3142 (6)	0.7497 (8)	-0.0351 (2)	0.064 (3)
C26	0.2938 (5)	0.7572 (8)	0.0016 (2)	0.048 (3)
C31	0.0517 (6)	0.7296 (8)	0.0563 (2)	0.037 (2)
C32	-0.0362 (6)	0.8037 (9)	0.0588 (2)	0.048 (2)
C33	-0.1297 (6)	0.7365 (9)	0.0547 (3)	0.064 (3)
C34	-0.1340 (7)	0.6046 (11)	0.0479 (2)	0.069 (3)
C35	-0.0485 (8)	0.5349 (10)	0.0455 (3)	0.072 (3)
C36	0.0462 (6)	0.5966 (9)	0.0503 (2)	0.055 (3)
C41	0.2285 (6)	0.8324 (8)	0.1869 (2)	0.035 (2)
C42	0.1546 (6)	0.8422 (10)	0.2117 (2)	0.062 (3)
C43	0.1395 (7)	0.9598 (12)	0.2293 (3)	0.071 (3)
C44	0.1983 (9)	1.0663 (11)	0.2233 (3)	0.074 (3)
C45	0.2721 (8)	1.0606 (9)	0.1992 (3)	0.062 (3)
C46	0.2875 (6)	0.9427 (9)	0.1814 (2)	0.052 (3)
C51	0.1414 (5)	0.5823 (8)	0.1650 (2)	0.036 (2)
C52	0.1374 (6)	0.4673 (8)	0.1853 (2)	0.051 (3)
C53	0.0494 (8)	0.3961 (9)	0.1859 (3)	0.071 (3)
C54	-0.0364 (8)	0.4391 (10)	0.1676 (3)	0.069 (3)
C55	-0.0357 (7)	0.5527 (11)	0.1471 (3)	0.074 (3)
C56	0.0510 (7)	0.6240 (9)	0.1457 (2)	0.064 (3)
C61	0.3434 (5)	0.5917 (8)	0.1938 (2)	0.036 (2)
C62	0.3890 (6)	0.4792 (8)	0.1812 (2)	0.045 (2)
C63	0.4522 (6)	0.4028 (8)	0.2049 (3)	0.053 (3)
C64	0.4701 (6)	0.4404 (10)	0.2409 (3)	0.059 (3)
C65	0.4276 (6)	0.5516 (10)	0.2536 (2)	0.056 (3)
C66	0.3641 (6)	0.6295 (8)	0.2299 (2)	0.045 (2)
C71	0.4877 (6)	0.9663 (7)	0.1131 (2)	0.033 (2)
C72	0.4102 (6)	1.0545 (8)	0.1030 (2)	0.045 (2)
C73	0.4217 (6)	1.1908 (8)	0.1077 (2)	0.052 (2)
C74	0.5108 (7)	1.2387 (8)	0.1234 (2)	0.051 (3)
C75	0.5868 (7)	1.1553 (9)	0.1348 (2)	0.055 (3)

C76	0.5768 (6)	1.0185 (8)	0.1296 (2)	0.040 (2)
C81	0.5580 (5)	0.7062 (8)	0.1336 (2)	0.033 (2)
C82	0.6216 (6)	0.6080 (9)	0.1232 (2)	0.053 (3)
C83	0.6839 (6)	0.5397 (9)	0.1486 (3)	0.066 (3)
C84	0.6843 (7)	0.5675 (9)	0.1855 (3)	0.061 (3)
C85	0.6213 (6)	0.6635 (9)	0.1963 (2)	0.058 (3)
C86	0.5573 (5)	0.7346 (8)	0.1712 (2)	0.045 (2)
C91	0.5280 (5)	0.7805 (8)	0.0580 (2)	0.029 (2)
C92	0.5692 (6)	0.8904 (8)	0.0422 (2)	0.042 (2)
C93	0.6133 (6)	0.8764 (9)	0.0091 (2)	0.054 (3)
C94	0.6208 (6)	0.7550 (9)	-0.0068 (2)	0.053 (3)
C95	0.5793 (6)	0.6471 (9)	0.0083 (2)	0.048 (2)
C96	0.5303 (5)	0.6586 (8)	0.0407 (2)	0.039 (2)
O1†	0.8524 (14)	0.1075 (18)	0.1689 (9)	0.210 (9)
C1	0.8524 (14)	0.1075 (18)	0.1689 (9)	0.210 (9)
C2	0.8448 (15)	0.076 (4)	0.2041 (8)	0.178 (10)
C3	0.8298 (14)	-0.058 (3)	0.2056 (7)	0.168 (8)
O4†	0.8585 (13)	-0.1174 (19)	0.1742 (10)	0.182 (9)
C4	0.8585 (13)	-0.1174 (19)	0.1742 (10)	0.182 (9)
C5	0.8792 (16)	-0.006 (5)	0.1517 (6)	0.199 (12)

† Occupancies: 19.1% O1 and 80.9% O4.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Cu—Cl	2.324 (2)	Cu—P1	2.346 (2)
Cu—P2	2.341 (2)	Cu—P3	2.352 (2)
Cl—Cu—P2	104.23 (8)	Cl—Cu—P3	101.47 (8)
Cl—Cu—P1	103.34 (8)	P2—Cu—P3	111.93 (8)
P2—Cu—P1	115.28 (8)	P1—Cu—P3	118.03 (8)

The position of the Cu atom was estimated using Patterson methods and all the remaining non-H-atom positions were estimated using subsequent Fourier syntheses. All non-H atoms were refined anisotropically and H atoms were inserted in calculated positions with common type-specific refined isotropic displacement parameters (phenyl: C—H = 0.93 \AA and $U_{\text{iso}} = 0.055 \text{\AA}^2$; tetrahydrofuran: C—H = 0.97 \AA and $U_{\text{iso}} = 0.252 \text{\AA}^2$); a riding model was used in the subsequent refinement. The solvent was found to be disordered, the O atom being distributed between the locations of atoms O1 and O4 only, with refined O-atom occupancies of 19.1 and 80.9%, respectively. No attempt was made to model the solvent as two molecules, however, since thermal motion of the solvent was in any case high. Anisotropic displacement parameters were retained for solvent non-H atoms in order to partially accommodate the variation in bond distances resulting from superposition of the two molecules.

Data collection: P3 (Siemens, 1982a). Data reduction: XTAPE (Siemens, 1982b). Program(s) used to solve structure: SHELXTL (Sheldrick, 1986). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diamminebis[dimethylglyoximato(1-)]cobalt(III) Fluoborate and Perchlorate

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Abstract

One of the title complexes, *trans*-diamminebis[2,3-butanedione dioximato(1-)]cobalt(III) tetrafluoroborate, $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{NH}_3)_2]\text{BF}_4$, is isomorphous with the other, *trans*-diamminebis[2,3-butanedione dioximato(1-)]cobalt(III) perchlorate, $[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{NH}_3)_2]\text{ClO}_4$. The octahedral coordination complex has an axial Co—N(NH₃) bond of 1.953 (2) (BF_4^- salt) or 1.954 (3) \AA (ClO_4^- salt).

Comment

When considering the biochemical reactions of the vitamin B₁₂ system, the Co—C bond cleavage step is of great interest (Finke, Schiraldi & Mayer, 1984). It has been revealed that the axial Co—C bond strength in the simple molecular models of vitamin B₁₂ is influenced by the ligand located in the opposite position, *i.e.* the 'structural *trans* effect' (Heeg, Elder & Deutsch, 1980). To define a 'zero' for this 'structural *trans* effect' series, the Co—N(NH₃) bond distance in the structures of *trans*-[(NH₃)₂Co(Hdmg)₂]X (where X = NO₃⁻, Br⁻