

Fig. 1. ORTEP plot showing 30% probability thermal ellipsoids.

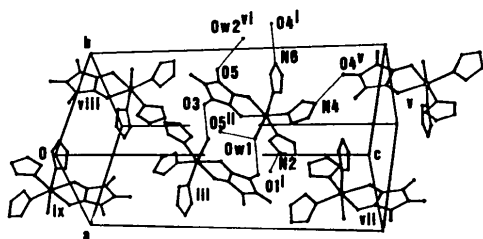


Fig. 2. An ORTEP view of the unit-cell contents with hydrogen-bonding scheme (fine lines). Symmetry operations are: (i)  $1 + x, y, z$ ; (ii)  $-x, 1 - y, 1 - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $-x, 1 - y, 1 - z$ ; (v)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (vi)  $1 + x, y, z$ ; (vii)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (viii)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (ix)  $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .

The metal atom is surrounded by a croconate molecule acting as chelating ligand, three imidazole molecules and one water molecule. In nickel croconate itself (Bottei, Chang & Lusardi, 1979) the complex is a one-dimensional polymer with the infinite chain resulting from the bonding of each metal to

two adjacent O atoms of one croconate and to a single oxygen atom of a second croconate molecule such that each croconate is three-coordinated.

In this compound, croconate is only two-coordinated as chelating nickel. The croconate ligand is planar although the C—C bond lengths suggest a partial localization of the  $\pi$  electrons. The C(5)—C(1) bond [ $1.416(4) \text{ \AA}$ ] is shorter than the other bonds in the ring [ $1.495(4)$  to  $1.444(5) \text{ \AA}$ ]. The Ni—N bonds are quite similar and it is not possible to discriminate between in plane and out of plane. The geometry of the imidazole ligand is similar to that reported earlier (Henrikson, 1977).

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## The Room- and Low-Temperature Structures of $(\varphi_4\text{As})\text{CuCl}_3$ , an Isolated, Non-Planar $\text{Cu}_2\text{Cl}_6^{2-}$ Ion

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**Abstract.** Tetraphenylarsonium trichlorocuprate(II),  $[\text{As}(\text{C}_6\text{H}_5)_4][\text{CuCl}_3]$ ,  $M_r = 553.2$ , monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $\text{Cu } K\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ),  $F(000) = 1108.0$ . The room-temperature structure (RT) has  $a = 9.289(3)$ ,  $b = 19.577(6)$ ,  $c = 13.464(5) \text{ \AA}$ ,  $\beta = 108.89(2)^\circ$ ,  $V = 2317(1) \text{ \AA}^3$ ,  $D_x = 1.58 \text{ g cm}^{-3}$ ,  $\mu = 63 \text{ cm}^{-1}$ ,  $R = 0.0474$  for 2154 unique observed [ $I \geq 3\sigma(I)$ ] reflec-

tions and 214 parameters. The low-temperature, 113 K, structure (LT) has  $a = 9.220(3)$ ,  $b = 19.494(5)$ ,  $c = 13.222(4) \text{ \AA}$ ,  $\beta = 108.65(2)^\circ$ ,  $V = 2252(1) \text{ \AA}^3$ ,  $D_x = 1.63 \text{ g cm}^{-2}$ ,  $\mu = 64 \text{ cm}^{-1}$ ,  $R = 0.0461$  for 2155 unique observed [ $I \geq 3\sigma(I)$ ] reflections and 214 parameters. At both temperatures, the  $[\text{Cu}_2\text{Cl}_6]^{2-}$  ion is isolated, with Cu atom geometries

Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for the  $\text{Cu}_2\text{Cl}_6^{2-}$  portion of tetraphenylarsonium trichlorocuprate(II): for each atom, first line is RT, second line LT

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U
As	6541 (1)	2067 (1)	4777 (1)	42 (1)
	6531 (1)	2069 (1)	4712 (1)	19 (1)
Cu	5190 (1)	452 (1)	8984 (1)	49 (1)
	5175 (1)	442 (1)	8947 (1)	22 (1)
Cl(1)	6757 (2)	61 (1)	595 (1)	60 (1)
	6762 (1)	82 (1)	611 (1)	27 (1)
Cl(2)	4333 (2)	252 (1)	7281 (1)	64 (1)
	4292 (2)	222 (1)	7210 (1)	28 (1)
Cl(3)	6387 (2)	1416 (1)	9002 (1)	77 (1)
	6377 (2)	1409 (1)	8929 (1)	32 (1)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for the  $\text{Cu}_2\text{Cl}_6^{2-}$  portion of tetraphenylarsonium trichlorocuprate(II)

	RT	LT
Cu—Cl(1)	2.328 (2)	2.327 (1)
Cu—Cl(2)	2.188 (2)	2.191 (2)
Cu—Cl(3)	2.291 (2)	2.289 (2)
Cu—Cl(1a)	2.212 (2)	2.220 (1)
Cl(3)—Cu—Cl(1a)	144.4 (1)	145.7 (1)
Cl(1)—Cu—Cl(3)	96.2 (1)	95.9 (1)
Cl(2)—Cu—Cl(1a)	97.2 (1)	96.9 (1)
Cl(1)—Cu—Cl(1a)	86.3 (1)	86.0 (1)
Cu—Cl(1)—Cu <sub>a</sub>	93.7 (1)	94.0 (1)
Cl(1)—Cu—Cl(2)	145.3 (1)	146.3 (1)
Cl(2)—Cu—Cl(3)	100.4 (1)	100.0 (1)

lying between square planar and tetrahedral, the average *trans* angle having a value of  $144.8^\circ$  for RT and  $146.0^\circ$  for LT. The terminal Cl atoms lie approximately  $1.25 \text{\AA}$  on either side of the  $\text{Cu}_2\text{Cl}_2$  bridging moiety. The  $\varphi_4\text{As}$  cations serve to isolate the dimers, with the shortest dimer-dimer contact being greater than  $6.5 \text{\AA}$ .

**Experimental.** An irregularly shaped, garnet red crystal, with the approximate dimensions  $0.20 \times 0.23 \times 0.31 \text{ mm}$ , was mounted on a thin glass fiber. The same crystal was used for both RT and LT structures. The crystals were obtained *via* evaporation of stoichiometric amounts of  $\varphi_4\text{AsCl}$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  from a hot concentrated HCl solution. The data were collected using an  $\omega$  scan, with a Nicolet R3m/E diffractometer with graphite monochromator. The diffractometer was configured as described by Campana, Shepard & Litchman (1981). The lattice constants of both structures were determined from 25 carefully centered Bragg reflections in the range  $60 \leq 2\theta \leq 63^\circ$ . Two check reflections,  $1\bar{1}0$  and  $\bar{1}03$ , were monitored every 100 reflections and showed no significant variation in either structure. An empirical absorption correction was applied assuming an ellipsoidally shaped crystal. This correction resulted in a

transmission range of  $0.448\text{--}0.929$  for RT and  $0.459\text{--}0.950$  for LT. The data were collected in the range  $3 \leq 2\theta \leq 100^\circ$  for both structures. For LT  $0 \leq h \leq 9$ ,  $0 \leq k \leq 19$  and  $-13 \leq l \leq 13$ . For RT  $0 \leq h \leq 9$ ,  $0 \leq k \leq 19$  and  $-13 \leq l \leq 13$ . A total of 2668 reflections for RT and 2600 for LT were collected, with 2154 unique observed [ $I \geq 3\sigma(I)$ ] reflections for RT and 2155 for LT. The RT and LT structures had merging *R* values of  $0.0804$  and  $0.0939$  respectively. The initial non-hydrogen thermal parameters for both structures were taken from the previous RT structure determined by Willett & Chow (1974). All H atoms were constrained, with C—H distances fixed at  $0.96 \text{\AA}$ , and thermal parameters fixed at  $0.08 \text{\AA}^2$ . The phenyl rings in the  $\varphi_4\text{As}$  cations were all constrained to be regular hexagons, with C—C  $1.395 \text{\AA}$ . The final refinement of 214 parameters resulted in  $R = 0.0474$  and  $R = 0.0461$  for RT and LT respectively. The final values of  $wR$ , with  $w = 1/[\sigma^2(F) + g(F)^2]$ , were  $wR = 0.0516$  and  $wR = 0.0523$  for RT and LT respectively. The final value of  $g$  was  $0.00139$  for RT and  $0.00179$  for LT. The goodness of fit was  $1.379$  for RT and  $1.337$  for LT. The values of  $|\Delta/\sigma|_{\text{max}}$  were  $0.005$  for RT and  $0.019$  for LT, with values of  $|\Delta/\sigma|_{\text{mean}}$  equal to  $0.001$  for RT and  $0.005$  for LT. The largest positive peaks appearing on the final difference maps for the two structures were  $0.75$  and  $1 \text{ e \AA}^{-3}$  for RT and LT respectively. The most negative peaks were  $0.8$  and  $0.9 \text{ e \AA}^{-3}$  for RT and LT respectively. *SHELXTL* software (Sheldrick, 1986) was used for data reduction and refinement. Atomic coordinates for both structures are listed in Table 1\* and bond distances and angles for both structures in Table 2. A view of the  $[\text{Cu}_2\text{Cl}_6]^{2-}$  ion showing the atomic numbering is given in Fig. 1.

\* Lists of structure factors, anisotropic thermal parameters, data collection parameters, atomic coordinates, bond lengths and angles, and H-atom parameters and a stereoview of the  $\text{Cu}_2\text{Cl}_6^{2-}$  ion have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53399 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

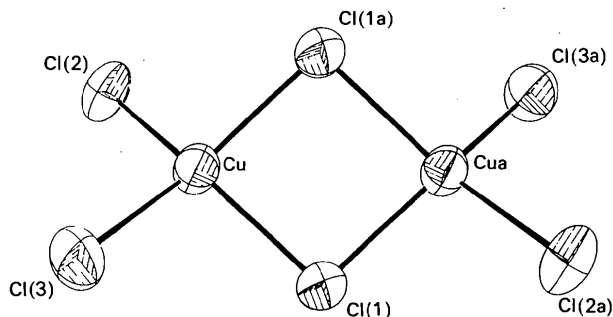


Fig. 1. A view of the  $[\text{Cu}_2\text{Cl}_6]^{2-}$  ion showing thermal ellipsoids.

**Related literature.** As mentioned in *Experimental*, the room-temperature structure determination was carried out previously by Willett & Chow (1974). The low-temperature structure was the main thrust of this work, and the room-temperature structure determination was performed only for purposes of comparison. The low-temperature structure determination was carried out in order to see if a significant structural difference existed between RT and LT, a question which was raised in an EPR study performed by Bencini, Gatteschi & Zanchini (1985).

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## Structure of a Chiral Iridium Bis(phosphine)–Diene Complex, a Catalyst for Homogeneous Hydrogenation

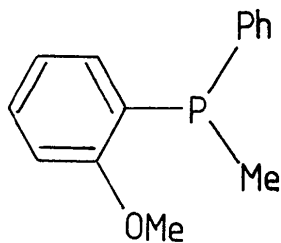
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**Abstract.** ( $\eta^4$ -1,5-Cyclooctadiene)bis[(*S*)-(2-methoxyphenyl)(methyl)(phenyl)phosphine]iridium(I) hexafluorophosphate,  $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{C}_{14}\text{H}_{15}\text{OP})_2][\text{PF}_6]$ ,  $M_r = 833.8$ , orthorhombic,  $C222_1$ ,  $a = 26.995$  (6),  $b = 22.122$  (5),  $c = 13.927$  (5) Å,  $V = 8316.9$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.33$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 33.6$  cm<sup>-1</sup>,  $F(000) = 3312$ ,  $T = 295$  K,  $R = 0.055$ ,  $wR = 0.074$  for 2501 reflections with  $|F^2| > 3\sigma(F^2)$ . The geometry at iridium is approximately square planar, with the expected distortions due to the size of the phosphine ligands: Ir—P1 2.320 (5), Ir—P2 2.323 (5) Å, P1—Ir—P2 92.3 (2), M1—Ir—P2 93.0, M1—Ir—M2 84.4, M2—Ir—P1 90.5° (M1 and M2 are the midpoints of the C1—C2 and C5—C6 bonds, respectively).

**Experimental.** The complex was prepared by the addition of (*S*)-(2-methoxyphenyl)(methyl)(phenyl)phosphine [(*S*)-pamp] [(1)] to  $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$



(1)

0108-2701/91/020437-03\$03.00

(Crabtree & Moorehouse, 1986) (cod = 1,5-cyclooctadiene, py = pyridine) and well formed crystals were obtained by diffusion of ether into a solution in dichloromethane. Data collected using a crystal  $ca$  0.25 × 0.25 × 0.2 mm, coated in epoxy glue, on an Enraf–Nonius CAD-4 diffractometer, monochromated Mo  $K\alpha$  radiation in the  $\theta$ – $2\theta$  mode, with  $\Delta\theta = (0.8 + 0.35\tan\theta)^\circ$  and a maximum scan time of 1 min. Cell parameters from setting angles of 25 reflections ( $7 \leq \theta \leq 10^\circ$ ). A total of 4017 unique reflections were measured for  $2 < \theta < 25^\circ$  and  $h$  0 → 32,  $k$  0 → 26,  $l$  0 → 16, and 2501 reflections with  $|F^2| > 3\sigma(F^2)$ , where  $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$ , were used in the refinement. Two reference reflections remeasured every 30 min showed no significant variation. An absorption correction was applied using *DIFABS* (Walker & Stuart, 1983), after isotropic refinement, and gave maximum and minimum corrections of 1.10 and 0.82. The structure was solved by routine heavy-atom methods and non-H atoms refined anisotropically (on  $F$ ) by full-matrix least squares. H atoms were held fixed at calculated positions with  $B_{\text{iso}} = 1.3 B_{\text{eq}}$  for the atoms to which they are bonded. With a weighting scheme of  $w = 1/\sigma^2(F)$ , the maximum shift/e.s.d. was 0.7, the final residuals were  $R = 0.055$  and  $wR = 0.074$ , 214 variables,  $\Delta\rho_{\text{max}} = 1.9$ ,  $\Delta\rho_{\text{min}} = -0.9$  e Å<sup>-3</sup>. The corresponding residuals for a refinement as the opposite absolute structure were  $R = 0.0673$ ,  $wR = 0.0897$ . Programs from the Enraf–Nonius *SDP-Plus* package