O(1)—V—N(1)	89.61 (8)	N(22)—C(21)—C(22)	122.1 (2)
O(1)—V—N(11)	96.92 (8)	C(2)—C(21)—C(22)	121.9 (2)
N(1)—V—N(11)	73.68 (7)	C(21)—C(22)—C(23)	119.0 (3)
V—N(1)—C(1)	103.2 (1)	C(22)—C(23)—C(24)	119.3 (3)
V—N(1)—C(2)	111.4 (1)	C(23)—C(24)—C(25)	118.1 (3)
V—N(1)—C(3)	109.3 (1)	N(22)—C(25)—C(24)	123.8 (3)
C(1)—N(1)—C(2)	109.6 (2)	N(1)—C(1)—C(11)	109.9 (2)
C(1)—N(1)—C(3)	110.5 (2)	N(1)—C(2)—C(21)	115.1 (2)
C(2)—N(1)—C(3)	112.5 (2)	N(11)—C(11)—C(1)	116.3 (2)
V—N(11)—C(11)	118.1 (1)	N(11)—C(11)—C(12)	121.6 (3)
V—N(11)—C(15)	122.6 (2)	C(1)—C(11)—C(12)	122.0 (2)
C(11)—N(11)—C(15)	119.0 (2)	O(1)—V—O(1^{i})	107.90 (2)
C(21)—N(22)—C(25)	117.7 (2)	O(1)—V—N(1^{i})	159.67 (1)
C(11)—C(12)—C(13)	118.8 (2)	O(1)—V—N(11^{i})	93.48 (1)
C(12)—C(13)—C(14)	119.8 (2)	N(1)—V—N(1^{i})	75.52 (1)
C(13)—C(14)—C(15)	118.4 (2)	N(1)—V—N(11^{i})	92.16 (7)
N(11)—C(15)—C(14)	122.3 (2)	N(11)—V—N(11^{i})	162.3 (1)
N(22)—C(21)—C(2)	116.0 (2)	N(1)—C(3)—C(3^{i})	110.2 (2)

Symmetry code: (i) $\frac{3}{2} - x, y, \frac{1}{2} - z$.

The title complex (1) was obtained from the reaction of $[V_2^{III}Cl_6(tpen)].2H_2O$ (Neves, Wieghardt, Nuber & Weiss, 1988) with tpen in a mixture of tetrahydrofuran and dimethylformamide at room temperature, whereby V^{III} is oxidized to V^{V} by air. The structure was solved by direct methods (Sheldrick, 1986) and subsequent difference Fourier synthesis. The least-squares refinement used anisotropic thermal parameters for the non-H atoms. The H atoms were not located on the ΔF map. The positions of the H atoms in phenyl groups were calculated and only included in the structure-factor calculations. Programs used were *VAXSDP* (version 3.0, 1986; Frenz, 1978) and *SHELXS*86 (*VMS* version; Sheldrick, 1986).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete bond distances, as well as packing diagrams, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71207 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1042]

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Tetramethylarsonium Pentachlorodicuprate(II)

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Abstract

The crystal structure of $(Me_4As)Cu_2Cl_5$ consists of two-dimensional $(Cu_2Cl_5^-)_\infty$ networks, lying parallel to the (101) plane of the monoclinic unit, separated by the Me_4As^+ cations. Each independent Cu^{II} ion has a distorted square-pyramidal geometry. The *anti*-apical site for Cu(2) is occupied by a Cl atom, Cl(4*a*), at a distance of 3.374 (1) Å, while the *anti*-apical site for Cu(1) is blocked by C(3) of the Me_4As^+ cation.

Comment

In an attempt to prepare an analog of the Jahn–Teller distorted $CsNiCl_3$ type structures found in $(Me_4N)CuCl_3$ (Bond, Willett, Haije & Maaskant, 1988), dilute HCl solutions containing 1:1, 1:1.5 or 1:2 mole ratios of Me_4AsCl and $CuCl_2$ were prepared. Slow evaporation yielded identical deep-red crystals from all three solutions.

The two-dimensional network (Fig. 1) can be envisioned as composed of undulating bibridged $(CuCl_2)_\infty$ chains running parallel to the [101] direction [defined by the Cu atoms Cu(2), Cu(1), Cu(2*b*), Cu(1*b*), Cu(2*d*), Cu(1*d*)]. These chains are linked by the Cl(3) atoms. The undulation of the chains is such that the apical Cu(1)—Cl(3) type bonds are external to the $(CuCl_2)_\infty$ chains, while the apical Cu(2)—Cl(5) type bonds lie in the chain. The undulations also lead to the existence of holes through the layer; each hole is capped by two Me_4As^+ ions in which the C(3) atoms point into the hole. More fundamentally, the structure can be related to the parent hexagonal CdI_2

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structure, in which the holes are due to the periodic loss of $Cu_2Cl_2^{2+}$ fragments. The high density of such holes apparently leads to the severe distortions observed in the layers. A similar loss of $Cu_2Cl_2^{2+}$ fragments has been observed in the structure of $(Et_3NMe)Cu_3Cl_7$ (Weise & Willett, 1993), but the lower density of holes leads to a much more recognizable relationship to the ferrodistortive $CuCl_2$ daughter structure of the CdI_2 structure.

The structure is isomorphous with the corresponding $(Me_4P)Cu_2Cl_5$ compound (Haije, Dobbelaar & Maaskant, 1986) with all Cu—Cl distances and angles identical between the two structures. ACu_2X_5 compounds (X = Cl, Br) with smaller cation/halide radius ratios form structures containing stacked quasi-planar $Cu_4X_{10}^{2-}$ oligomers (Geiser, Willett, Lindbeck & Emerson, 1986; Caputo, Vukosavovich & Willett, 1976; Murray & Willett, 1991).

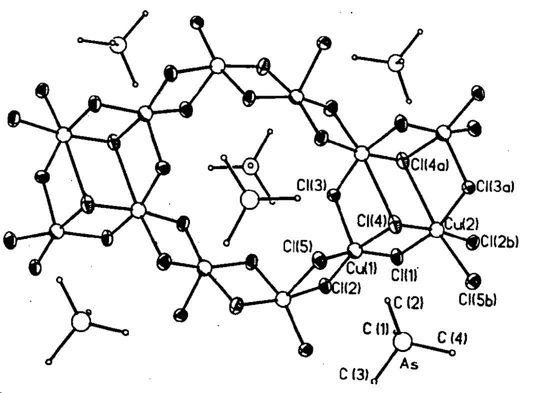

Fig. 1. Illustration of the structure of $(Me_4As)Cu_2Cl_5$. Large open circles, As; small open circles, C; intermediate open circles, Cu(2); intermediate shaded circles, Cu(1).

Experimental

Crystal data

$[As(CH_3)_4][Cu_2Cl_5]$
M_r = 439.4
Monoclinic
$P2_1/n$
a = 10.197 (2) Å
b = 12.007 (3) Å
c = 11.075 (2) Å
β = 110.16 (2)°
V = 1272.3 (5) Å^3
Z = 4
D_x = 2.29 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 33–38°
μ = 6.95 mm^{-1}
T = 20 K
Platelets
0.39 × 0.24 × 0.08 mm
Red

Data collection

Upgraded $P2_1$ diffractometer
ω scans

$R_{\rm int}$ = 0.0568
$\theta_{\max}$ = 30°

Absorption correction: empirical
$T_{\min}$ = 0.312, $T_{\max}$ = 0.460
4053 measured reflections
3702 independent reflections
3307 observed reflections [$|F|>3\sigma(F)$]

h = 6 → 14
k = 0 → 16
l = 0 → 15
2 standard reflections monitored every 96 reflections
intensity variation: 2%

Refinement

Refinement on F
Final R = 0.0417
wR = 0.0594
S = 1.581
3307 reflections
110 parameters
$w = 1/[\sigma^2(F) + 0.0074(F)^2]$
$(\Delta/\sigma)_{\max}$ = 1.147
$\Delta\rho_{\max}$ = 1.0 e Å^{-3}
$\Delta\rho_{\min}$ = −0.9 e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 1990)
Extinction coefficient: 0.00038
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) *with e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$
Cu(1)	0.6398 (1)	0.2947 (1)	0.6350 (1)	0.027 (1)
Cu(2)	0.3771 (1)	0.3814 (1)	0.3615 (1)	0.028 (1)
Cl(1)	0.4014 (1)	0.2746 (1)	0.5408 (1)	0.035 (1)
Cl(2)	0.6402 (1)	0.1598 (1)	0.7854 (1)	0.035 (1)
Cl(3)	0.6409 (1)	0.4699 (1)	0.7688 (1)	0.036 (1)
Cl(4)	0.6172 (1)	0.3967 (1)	0.4496 (1)	0.036 (1)
Cl(5)	0.8701 (1)	0.2680 (1)	0.6800 (1)	0.037 (1)
As	0.2241 (1)	0.4528 (1)	0.8249 (1)	0.035 (1)
C(1)	0.3439 (6)	0.5771 (4)	0.8845 (5)	0.047 (2)
C(2)	0.3332 (7)	0.3211 (5)	0.8517 (6)	0.055 (2)
C(3)	0.1010 (6)	0.4472 (4)	0.9191 (5)	0.043 (2)
C(4)	0.1215 (6)	0.4680 (5)	0.6463 (5)	0.054 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu(1)—Cl(1)	2.303 (1)	Cu(2)—Cl(4)	2.310 (1)
Cu(1)—Cl(2)	2.322 (1)	Cu(2)—Cl(2$^{\rm i}$)	2.321 (1)
Cu(1)—Cl(3)	2.570 (1)	Cu(2)—Cl(3$^{\rm ii}$)	2.262 (1)
Cu(1)—Cl(4)	2.332 (1)	Cu(2)—Cl(5$^{\rm i}$)	2.677 (1)
Cu(1)—Cl(5)	2.250 (1)	Cu(2)—Cl(4$^{\rm ii}$)	3.374 (1)
Cu(2)—Cl(1)	2.304 (1)		
Cl(1)—Cu(1)—Cl(2)	89.6 (1)	Cl(1)—Cu(2)—Cl(3$^{\rm ii}$)	161.7 (1)
Cl(1)—Cu(1)—Cl(3)	98.1 (1)	Cl(4)—Cu(2)—Cl(3$^{\rm ii}$)	92.8 (1)
Cl(2)—Cu(1)—Cl(3)	99.1 (1)	Cl(2$^{\rm i}$)—Cu(2)—Cl(3$^{\rm ii}$)	95.2 (1)
Cl(1)—Cu(1)—Cl(4)	83.6 (1)	Cl(1)—Cu(2)—Cl(5$^{\rm i}$)	104.0 (1)
Cl(2)—Cu(1)—Cl(4)	166.5 (1)	Cl(4)—Cu(2)—Cl(5$^{\rm i}$)	96.9 (1)
Cl(3)—Cu(1)—Cl(4)	93.3 (1)	Cl(2$^{\rm i}$)—Cu(2)—Cl(5$^{\rm i}$)	80.1 (1)
Cl(1)—Cu(1)—Cl(5)	160.6 (1)	Cl(3$^{\rm ii}$)—Cu(2)—Cl(5$^{\rm i}$)	94.2 (1)
Cl(2)—Cu(1)—Cl(5)	89.9 (1)	Cu(1)—Cl(1)—Cu(2)	96.6 (1)
Cl(3)—Cu(1)—Cl(5)	101.1 (1)	Cu(1)—Cl(2)—Cu(2$^{\rm iii}$)	98.9 (1)
Cl(4)—Cu(1)—Cl(5)	92.8 (1)	Cu(1)—Cl(3)—Cu(2$^{\rm ii}$)	107.1 (1)
Cl(1)—Cu(2)—Cl(4)	84.1 (1)	Cu(1)—Cl(4)—Cu(2)	95.7 (1)
Cl(1)—Cu(2)—Cl(2$^{\rm i}$)	89.1 (1)	Cu(1)—Cl(5)—Cu(2$^{\rm iii}$)	91.0 (1)
Cl(4)—Cu(2)—Cl(2$^{\rm i}$)	171.7 (1)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The *SHELXTL* (Sheldrick, 1990) crystallographic program package (Sheldrick, 1990) was utilized for data reduction and refinement. Initial Cu-, As- and Cl-atom positions were taken from the isomorphous $(Me_4P)Cu_2Cl_5$ structure (Haije, Dobbelaar & Maaskant, 1986). A difference synthesis based on these positions yielded the C-atom positions. H atoms were constrained to ideal positions (C—H = 0.96 Å) and assigned isotropic thermal parameters with magnitudes 1.2 times greater than those of the associated C atoms. Refinement proceeded in a straightforward fashion.

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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 71255 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1031]

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Heptacarbonylbis(triphenylphosphine)-bis(μ_3-tellurium)-triiron

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Abstract

The heptacarbonyl-1κ^3C,2κ^2C,3κ^2C-bis(μ_3-tellurido)-bis(triphenylphosphine)-2κP,3κP-triiron, $(PPh_3)_2$-$Fe_3(CO)_7(\mu_3\text{-}Te)_2$, structure is a distorted square-pyramid motif with three Fe and two Te atoms at the vertices; Fe(1), Fe(2), Te(1) and Te(2) form the base of the pyramid with Fe(1)—Te(1) = 2.531 (1), Fe(1)—Te(2) = 2.544 (1), Fe(2)—Te(1) = 2.539 (1) and Fe(2)—Te(2) = 2.549 (1) Å. Fe(1) and Fe(2) have two terminal carbonyl ligands and one triphenylphosphine ligand; the phosphine ligands are coordinated equatorially to Fe(1) and axially to Fe(2). The apical Fe(3) atom has three terminal carbonyl ligands.

Comment

The most striking feature of the title complex is the presence of both equatorially and axially coordinated phosphine ligands. This same axial–equatorial coordination scheme was also observed in $(PPh_3)_3$-$Ru_3(CO)_6(\mu_3\text{-}Te)_2$ (Mathur, Thimmappa & Rheingold, 1990) which contains a third phosphine ligand on an apical Ru atom. However, previous reports of structures containing a similar metal-chalcogen cluster framework indicate a preference for equatorial coordination of bulky ligands: $(C_3Ph_2)Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Dettlaf, Hubener, Klimes & Weiss, 1982), $(C_3H_2S_2)Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Benoit, Marouille & Patin, 1982) and (Me_2NH)-$Fe_3(CO)_8(\mu_3\text{-}S)_2$ (Adams & Babin, 1986). Comparing the bond lengths of the phosphine ligands reveals, however, that the axial triphenylphosphine ligand has the shorter bond: the axial Fe(2)—P(2) bond is 2.214 (1) Å and the equatorial Fe(1)—P(1) bond is 2.274 (1) Å. The axial Fe(1)—C(2) carbonyl bond length at 1.749 (4) Å is *shorter* than the equatorial Fe(1)—C(1) carbonyl bond at 1.792 (3) Å. [The two Fe(2) carbonyl ligands are statistically identical and of an intermediate length with an averaged bond distance of 1.777 (3) Å.] The structure also shows that equatorial triphenylphosphine ligation places stress on the apical Fe(3) position: the Fe(3)—Fe(1) distance, 2.800 (1) Å, is much longer than the

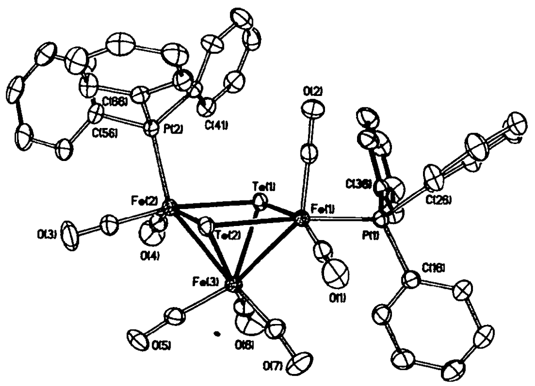

Fig. 1. Diagram for $(PPh_3)_2Fe_3(CO)_7(\mu_3\text{-}Te)_2$ showing the numbering scheme. Thermal ellipsoids are drawn at 35% probability boundaries.

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