Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $CoSb_3$; *figures in square brackets data for specimen* 2, *in curly brackets data from Kjekshus & Rakke* (1974)

Sb—Sb	2·8540 (6)		[2·8799 (8)]	{2·891}
	2·9760 (6)		[2·9836 (9)]	{2·982}
	3·4322 (5)	4×	[3·4396 (6)]	
	3·7146 (5)	4×	[3·7336 (7)]	
Co—Sb	2·5287 (3)	6×	[2·5382 (4)]	{2·520}
Co—Co	4·5192 (2)	6×	[4·5388 (3)]	{4·517} = *a*/2
Sb—Co—Sb	85·47 (1)	6×	[85·31 (1)]	{ 85·3}
Sb—Co—Sb	94·53 (1)	6×	[94·69 (1)]	{ 94·7}
Co—Sb—Sb	107·77 (1)	2×	[107·84 (1)]	{107·7}
Co—Sb—Sb	109·22 (1)	2×	[109·07 (1)]	{108·8}
Co—Sb—Co	126·65 (2)		[126·78 (1)]	{127·3}
Sb—Sb—Sb	90·00 (1)		[90·00 (1)]	{ 90·0}

[figure given among others in Lutz & Kliche (1981)], is confirmed. The Co—Sb, Sb—Sb and Co—Co distances are given in Table 2. The shortest intermolecular Sb—Sb distances, *i.e.* 3·4322 (5) [3·4396 (6)] Å, are even smaller than those calculated from the van der Waals radii of the smaller atoms As or P [3·70 and 3·60 Å, respectively (Bondi, 1964)]. The unit-cell dimensions of the crystals studied are somewhat larger than those of powdery material, *i.e.* 9·0385 (3) [9·0775 (6)] instead of 9·0356 (6) (this work) and 9·0347 (6) Å (Kjekshus & Rakke, 1974). These findings are possibly due to incorporation of the transport agents Cl and I, respectively.

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Structure of Di-μ-chloro-bis(dicarbonylpalladium)*

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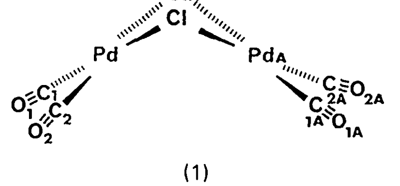
Abstract. $[Pd_2Cl_2(CO)_4]$, $M_r = 395·8$, tetragonal, $I\bar{4}2d$, $a = 14·279$ (9), $b = 14·279$ (9), $c = 9·280$ (5) Å, $V = 1892$ (2) Å^3, $Z = 8$, $D_x = 2·78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7071$ Å, $\mu = 4·297$ mm^{-1}, $F(000) = 1456$, $T = 293$ K, $R = 0·033$ for 535 observed reflections with $I > 2·5\sigma(I)$. The structure consists of discrete dimeric molecules formed by two deformed square-planar arrangements around the Pd atoms joined at a common edge, with bridging chlorines equally shared between the Pd atoms. The Pd—Cl distances are 2·387 (3) and 2·371 (2) Å; the Pd—Pd intramolecular distance is 3·114 (2) Å.

Introduction. As part of a study of metal carbonyl halides, the title compound (1) was synthesized from the reaction of $PdCl_2$ (420 mg, 2·36 mmol), $NaHCO_3$ (780 mg, 9·5 mmol) and anhydrous methanol (100 ml) in the presence of 2-(1,5-dimethyl-4-hexenyl)-3-hydroxy-5-methyl-1,4-benzoquinone (perezone) (460 mg, 196 mmol). The reaction vessel was purged with dry nitrogen and carbon monoxide was then passed through the stirred solution for 6 h at 343 K. The reaction product was isolated and recrystallized from degassed *n*-hexane to give air-stable crystals. IR (KBr pellets): 2103 *m*, 2082 *s*, 2024 *vs* and 1997 *w* cm^{-1}. The structure determination was undertaken to elucidate the stereochemistry of (1).



(1)

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Experimental. Red prismatic crystal $0{\cdot}34 \times 0{\cdot}34 \times 0{\cdot}54$ mm. Nicolet *R*3 four-circle diffractometer, graphite-monochromated Mo*Kα* radiation. Lattice parameters from 20 machine-centred reflections with $5{\cdot}2 < 2\theta < 22{\cdot}1°$, 561 reflections ($h0\rightarrow18$, $k0\rightarrow18$, $l0$–12, $2\theta < 55°$), 535 independent with $I > 2{\cdot}5\sigma(I)$, $2\theta/\theta$-scan mode, variable scan speed, scan width 1·0° (θ), two standard reflections ($0\bar{4}\bar{2}$, $23\bar{3}$) monitored every 50 measurements, Lp correction, empirical absorption correction based on reflection intensity measurements at different azimuthal angles, transmission range 0·10–0·23. Structure solved by heavy-atom method. Least-squares refinement with all atoms treated anisotropically. $\sum w|\Delta F|^2$ minimized with $w = [\sigma^2(F_o) + 0{\cdot}00005(F_o)^2]^{-1}$, where σ is the standard deviation of observed amplitudes based on counting statistics; isotropic extinction parameter $X = -0{\cdot}0002$; $S = 0{\cdot}95$. In the last cycle $(\Delta/\sigma)_{\max} = 0{\cdot}105$, residual electron density within $-0{\cdot}40$ and $0{\cdot}60$ e Å^{-3}. Final $R = 0{\cdot}033$, $wR = 0{\cdot}030$. Scattering factors from *International Tables for X-ray Crystallography* (1974). All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with *SHELXTL* (Sheldrick, 1981).

Discussion. Final positional parameters and equivalent isotropic temperature factors are given in Table 1.* The molecular structure of (1) is shown in Fig. 1 and consists of dimeric molecules separated by normal van der Waals contacts; only the crystallographically unique atoms in the figure are labelled. The intramolecular distances and bond angles are given in Table 2. Each molecular unit (Fig. 1) consists of two distorted square-planar ClPd(CO)$_2$ units, joined at a common edge *via* the bridging Cl atoms, which are shared equally between the Pd atoms.

The Pd—Cl bond lengths of 2·387 (3) and 2·371 (2) Å are shorter than the values of 2·422 (7) and 2·426 (5) Å in bis(2-neopentyl-η-allylpalladium chloride).2CHCl$_3$ (Murphy, Holt & Holt, 1981), and 2·492 (2) and 2·474 (2) Å in bis(μ-chloro)-bis[2-(di-*tert*-butylphosphino)-2-methylpropyl]dipalladium (Oliver, Mullica & Milligan, 1982). However, the bond angles Pd—Cl—Pd(*A*) and Pd—Cl(*A*)—Pd(*A*) are in good agreement with values in the literature cited above.

The mean Pd—C bond length of 1·852 (10) Å is significantly shorter than the values 2·023 (6) and 2·052 (8) Å found in di-μ-chloro-bis[(3-hydroxyimino-2,2-dimethylbutyl-C^1,N)-palladium(II)] (Constable, McDonald, Sawkins & Shaw, 1980) and bis(μ-chloro)-bis[2-(di-*tert*-butylphosphino)-2-methylpropyl]-dipalladium (Oliver, Mullica & Milligan, 1982), respectively. However, the mean C—O bond length of 1·089 (14) Å is reasonably close to the mean C—O

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3)

$$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\rm eq}$
Pd	1480 (1)	2289 (1)	4604 (1)	65 (1)
Cl	2035 (2)	3611 (2)	5926 (2)	76 (1)
C(1)	1056 (7)	1206 (8)	3646 (10)	72 (3)
O(1)	860 (7)	566 (8)	3139 (8)	103 (4)
C(2)	936 (7)	3013 (9)	3223 (8)	77 (4)
O(2)	590 (7)	3463 (9)	2401 (8)	122 (5)

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

Pd—Cl	2·387 (3)	Pd—C(1)	1·883 (11)
Pd—C(2)	1·821 (10)	Pd—Cl(*A*)	2·371 (2)
Cl—Pd(*A*)	2·371 (2)	C(1)—O(1)	1·066 (15)
C(2)—O(2)	1·113 (14)		
Cl—Pd—C(1)	177·0 (3)	Cl—Pd—C(2)	93·1 (4)
C(1)—Pd—C(2)	89·8 (5)	Cl—Pd—Cl(*A*)	85·5 (1)
C(1)—Pd—Cl(*A*)	91·5 (3)	C(2)—Pd—Cl(*A*)	173·3 (3)
Pd—Cl—Pd(*A*)	81·8 (1)	Pd—C(1)—O(1)	175·7 (10)
Pd—C(2)—O(2)	178·4 (9)		

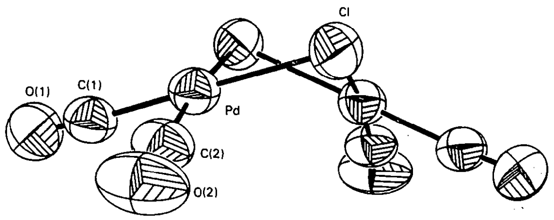

Fig. 1. The molecular conformation of di-μ-chloro-bis(dicarbonylpalladium) showing the atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

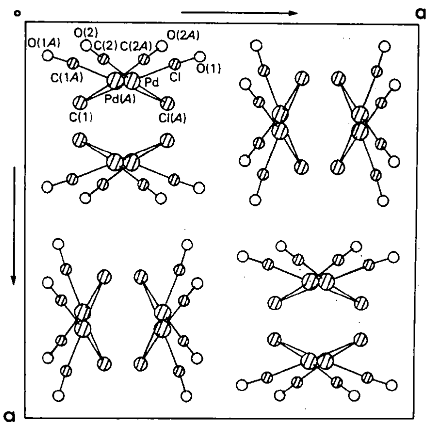

Fig. 2. Projection of the structure along **c**.

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* Lists of structure amplitudes, anisotropic thermal parameters and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44020 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

value of 1·17 (1) Å, found in the isostructural $[Rh_2Cl_2(CO)_4]$ compound (Dahl, Martell & Wampler, 1961).

The Pd^{II} atom lies in an approximate distorted square-planar environment. The angles C(1)—Pd—C(2), C(2)—Pd—Cl and Cl—Pd—Cl(*A*) are close to 90° at 89·8 (5), 93·1 (4) and 85·5 (1)°, respectively. The dihedral angle between $PdCl(CO)_2$ groups is 121·9 (4)° in agreement with the dihedral angle (124°) reported for the isostructural $[Rh_2Cl_2(CO_4)]$ compound.

The packing of the dimeric molecules in the unit cell is shown in Fig. 2. The discrete dimeric molecules are held in the crystal by van der Waals and packing forces. There is only one Pd—Pd intermolecular contact of 3·317 (2) Å $(0{\cdot}5-x, y, 0{\cdot}75-z)$.

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Structure of $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$

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Abstract. $M_r = 1453{\cdot}75$, monoclinic, $C2/c$, $a = 20{\cdot}3058$ (20), $b = 11{\cdot}7172$ (18), $c = 25{\cdot}3984$ (15) Å, $\beta = 117{\cdot}201$ (6)°, $V = 5375$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}80$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 16{\cdot}60$ cm^{-1}, $F(000) = 2944$, $T = 298$ K, $R = 0{\cdot}0328$ for 2921 observed reflections. The reaction of $TiCl_4$ with water vapor produced colorless crystals that have been found to contain Ti atoms coordinated by water and oxide to form a cubic octamer. The average O—Ti—O bond angle is 99·55° [range 97·51 (8)–102·35 (9)°] and the average Ti—O bond distance is 1·820 Å [1·791 (2)–1·859 (2) Å]. The average Ti—O—Ti angle is 154·60° [153·10 (11)–156·03 (11)°]. The average Ti—OH_2 bond distance is 2·129 Å [2·081 (2)–2·179 (2) Å] and the average H_2O—Ti—OH_2 bond angle is 79·52° [78·51 (7)–80·95 (8)°]. The average axial octahedral H_2O—Ti—O angle is 164·57° [162·25 (8)–166·23 (8)°].

Introduction. A titanium hydroxychloride produced from the reaction of $TiCl_4$ with H_2O has been examined previously and the powder X-ray diffraction pattern reported (Walter-Levy & Ferey, 1968). The empirical formula was determined by elemental analysis to be $TiCl(OH)_3.2H_2O$ (Walter-Levy & Ferey, 1966; Golub, Tischenko & Kikot, 1970). We have isolated single crystals from this reaction and have characterized them as $[Ti_8O_{12}(H_2O)_{24}]Cl_8.HCl.7H_2O$. The powder XRD pattern of these crystals matches that previously reported for '$TiCl(OH)_3.2H_2O$'.

Experimental. Small irregular colorless crystals were discovered in the center of clumps of powder obtained by reaction of $TiCl_4$ with moist air. Fragments were selected by optical examination and mounted on glass fibers using polycyanoacrylate cement. They were then coated with this cement to prevent further reaction with the air.

X-ray data were obtained with an Enraf–Nonius CAD-4 diffractometer. The approximate dimensions of the crystal were 0·19 × 0·20 × 0·30 mm. The 2θ range was $2 < 2\theta < 45°$, $+h(0,21)$, $+k(0,12)$, $\pm l(-27,27)$,

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