Fig. 1. Projection de la structure de $(NH_4)_2H_2CH_2P_2O_6$ dans le plan *xyO*.

mesurées. Une corection d'absorption a été effectuée sur le composé au thallium à l'aide du programme *AGNOST* (Ahmed, 1974). Pas de correction d'extinction secondaire.

La structure est résolue par *MULTAN* (Germain, Main & Woolfson, 1971). Les atomes d'hydrogène sont localisés sur des 'sections différences' et affinés avec un facteur d'agitation thermique isotrope. Dans le cas du composé au thallium le facteur d'agitation thermique des atomes d'hydrogène a été fixé à $1,5 \text{ Å}^2$; les positions de ces atomes n'ont pu être affinées. Les facteurs de diffusion sont extraits des *International Tables for X-ray Crystallography* (1974). Des détails additionnels sont donnés dans le Tableau 1.

Les paramètres atomiques sont donnés dans les Tableaux 2 et 3, les distances et angles caractéristiques dans les Tableaux 4 et 5.*

Littérature associée. La structure du composé à l'ammonium (Fig. 1) est constituée de chaînes infinies $(HPO_3-CH_2-PO_3H)^{2-}$ reliées entre elles par les ions NH_4^+ dans un système de liaisons hydrogènes tridimensionnel. Celle du composé au thallium est tout à fait analogue.

Références

AHMED, F. U. (1974). *Crystallographic Computing Techniques*, p. 271. Copenhagen: Munksgaard.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–379.
HMIMID, N., BESSE, J. P. & CHEVALIER, R. (1985). *Mater. Chem. Phys.* 12, 491–496.
International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

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trans-Carbonylchlorobis(triphenylphosphine)rhodium(I), a New Polymorph

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Abstract. $[RhCl(CO)\{P(C_6H_5)_3\}_2]$, $M_r = 690.91$, monoclinic, $P2_1/n$, $a = 11.968$ (3), $b = 24.505$ (7), $c = 12.191$ (4) Å, $\beta = 113.27$ (2)°, $V = 3285$ (2) Å^3, $Z = 4$, $D_x = 1.40$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 7.1$ cm^{-1}, $F(000) = 1408$, $T = 293$ K, $R_F = 3.70\%$ for 3997 observed reflections and 308 parameters. The structure is similar to one previously reported as a noncentrosymmetric triclinic polymorph with 'implausible' bond lengths. The Rh^I coordination environment is square planar; the maximum deviation

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[0·06 (1) Å] from planarity is at the carbonyl C atom. Rh—C 1·821 (5), Rh—Cl 2·395 (1), Rh—P 2·333 (1) and 2·327 (1) Å.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
Rh	1852·7 (3)	1467·8 (1)	5147·8 (3)	48 (1)
P(1)	1939 (1)	1632 (1)	7065 (1)	48 (1)
P(2)	1705 (1)	1247 (1)	3239 (1)	46 (1)
Cl	2075 (1)	512 (1)	5593 (1)	58 (1)
O(1)	1831 (4)	2650 (1)	4640 (4)	103 (2)
C(1)	1809 (4)	2194 (2)	4822 (4)	67 (2)
C(11)	1186 (2)	2707 (1)	7084 (2)	69 (2)
C(12)	1329	3254	7429	79 (3)
C(13)	2444	3440	8260	84 (3)
C(14)	3417	3078	8746	78 (2)
C(15)	3274	2531	8402	59 (2)
C(16)	2159	2346	7571	51 (2)
C(21)	3052 (3)	1085 (1)	9269 (3)	73 (2)
C(22)	4041	845	10184	101 (3)
C(23)	5156	799	10079	112 (3)
C(24)	5283	993	9059	109 (3)
C(25)	4295	1233	8143	90 (3)
C(26)	3179	1279	8249	56 (2)
C(31)	−184 (3)	1015 (1)	6504 (2)	62 (2)
C(32)	−1273	865	6585	76 (2)
C(33)	−1648	1127	7398	83 (3)
C(34)	−934	1539	8130	82 (3)
C(35)	155	1690	8049	70 (2)
C(36)	530	1428	7236	52 (2)
C(41)	78 (3)	813 (1)	1072 (2)	75 (2)
C(42)	−920	504	348	92 (3)
C(43)	−1619	225	850	87 (3)
C(44)	−1320	255	2076	77 (2)
C(45)	−322	564	2801	62 (2)
C(46)	377	843	2299	50 (2)
C(51)	2931 (3)	364 (1)	2711 (3)	73 (2)
C(52)	3976	71	2844	102 (4)
C(53)	5117	265	3601	100 (3)
C(54)	5212	752	4226	99 (3)
C(55)	4166	1044	4093	79 (2)
C(56)	3026	850	3336	50 (2)
C(61)	2562 (2)	1940 (1)	1855 (3)	69 (2)
C(62)	2440	2378	1086	86 (3)
C(63)	1386	2695	693	89 (3)
C(64)	454	2574	1069	94 (3)
C(65)	576	2135	1838	75 (2)
C(66)	1630	1818	2230	53 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Experimental. Yellow crystals (0·25 × 0·25 × 0·30 mm). Nicolet $R3m$ diffractometer, ω scans, lattice parameters from least-squares fit of 25 reflections, $20 \le 2\theta \le 25°$, absorption correction unnecessary ($\mu = 7·1$ cm^{-1}, uniform shape, $T_{max}/T_{min} = 1·08$), $2\theta_{max} = 48°$ ($h = \pm 14$, $k = +29$, $l = +14$), standard reflections $\bar{4}56$, $\bar{2},12,1$, $\bar{6}11$, ≤1% decay, 5449 reflections collected, 5133 unique, $R_{int} = 2·71\%$, 1136 unobserved reflections, 3997 reflections with $F_o \ge 5\sigma(F_o)$, direct-methods (*SOLV*) solution, refinement on F for 308 parameters, phenyls constrained to fit rigid hexagons [d(C—C) = 1·395 Å], all non-H atoms anisotropic, H atoms calculated and fixed in idealized positions [d(C—H) = 0·96 Å, $U = 1·2U$ of attached C], $R_F = 3·70\%$, $wR_F = 4·21\%$, $S = 1·281$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0·0008$, $(\Delta/\sigma)_{max} = 0·067$, $(\Delta\rho)_{max} = 0·42$ e Å^{-3}, $(\Delta\rho)_{min} = -0·34$ e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: Sheldrick (1984).*

Atomic parameters are given in Table 1, bond lengths and angles in Table 2. Fig. 1 shows the molecular structure and labeling scheme.

Related literature. Del Pra, Zanotti & Segala (1979) have reported the structure of a noncentrosymmetric triclinic polymorph of the title compound. However, the presence of anomalous bond distances [*e.g.* a C—O carbonyl distance of 0·74 (1) Å and significantly different Rh—P distances, 2·363 (2) and 2·304 (2) Å] and inversionally related coordinates for related atoms

Table 2. *Bond lengths* (Å) *and angles* (°)

Rh—P(1)	2·333 (1)	Rh—P(2)	2·327 (1)
Rh—Cl	2·395 (1)	Rh—C(1)	1·821 (5)
P(1)—C(16)	1·839 (3)	P(1)—C(26)	1·828 (3)
P(1)—C(36)	1·848 (4)	P(2)—C(46)	1·839 (3)
P(2)—C(56)	1·820 (3)	P(2)—C(66)	1·842 (3)
O(1)—C(1)	1·141 (6)		
P(1)—Rh—P(2)	176·1 (1)	P(1)—Rh—Cl	89·1 (1)
P(2)—Rh—Cl	87·5 (1)	P(1)—Rh—C(1)	92·1 (2)
P(2)—Rh—C(1)	91·4 (2)	Cl—Rh—C(1)	175·5 (2)
Rh—P(1)—C(16)	116·4 (1)	Rh—P(1)—C(26)	114·2 (1)
Rh—P(1)—C(36)	112·7 (1)	Rh—P(2)—C(46)	117·0 (1)
Rh—P(2)—C(56)	109·8 (1)	Rh—P(2)—C(66)	117·1 (1)
Rh—C(1)—O(1)	177·2 (4)	P(1)—C(16)—C(11)	118·5 (1)
P(1)—C(16)—C(15)	121·5 (1)	P(1)—C(26)—C(21)	121·6 (1)
P(1)—C(26)—C(25)	118·3 (1)	P(1)—C(36)—C(31)	118·7 (1)
P(1)—C(36)—C(35)	121·3 (1)	P(2)—C(46)—C(41)	119·3 (1)
P(2)—C(46)—C(45)	120·7 (1)	P(2)—C(56)—C(51)	122·7 (1)
P(2)—C(56)—C(55)	117·3 (1)	P(2)—C(66)—C(61)	123·2 (1)
P(2)—C(66)—C(65)	116·8 (1)		
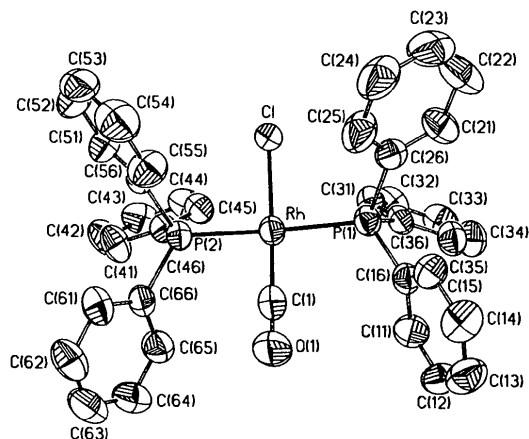
Fig. 1. Molecular structure and labeling scheme for [RhCl(CO){P(C₆H₅)₃}₂]. H atoms are deleted for clarity.

suggests an incorrect space-group assignment. The presence of an inversion center would produce chloride–carbonyl disorder, a not uncommon phenomenon.

Crystals of the title compound were the gift of Dr Donald J. Darensbourg, Texas A & M University.

References

DEL PRA, A., ZANOTTI, G. & SEGALA, P. (1979). *Cryst. Struct. Commun.* **8**, 959–964.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
SHELDRICK, G. M. (1984). *SHELXTL Program Library*, version 4.1. Nicolet XRD Corporation, Madison, Wisconsin.

Structure of Tetrakis(tetraphenylphosphonium) Octakis[chlorocopper(I)]bis[tetrathiotungstate(VI)]*

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Abstract. $[P(C_6H_5)_4]_4[\{WS_4(CuCl)_4\}_2]$, $M_r = 2773\cdot8$, triclinic, $P\bar{1}$, $a = 13\cdot068$ (1), $b = 14\cdot361$ (1), $c = 15\cdot556$ (1) Å, $\alpha = 109\cdot458$ (6), $\beta = 93\cdot626$ (6), $\gamma = 108\cdot724$ (4)°, $V = 2559\cdot2$ Å^3, $Z = 1$, $D_x = 1\cdot799$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 4\cdot39$ mm^{-1}, $F(000) = 1360$, $T = 293$ K. $R = 0\cdot033$ for 7180 unique observed reflections. In the dimeric anion, each W atom is tetrahedrally coordinated by S [W–S = 2·222 (2)–2·248 (2) Å]; six of the Cu atoms have trigonal-planar coordination, with bonds to two μ_3-S^{2-} ligands [Cu–S = 2·253 (2)–2·267 (2) Å] and one terminal Cl$^-$ ligand [Cu–Cl = 2·130 (2)–2·151 (2) Å]. Distorted tetrahedral coordination of the other two Cu atoms is completed by formation of two asymmetrical μ_2-Cl bridges across an inversion centre [Cu–Cl = 2·272 (2), 2·436 (2) Å, Cu–S = 2·293 (2), 2·318 (2) Å, Cu–Cl–Cu = 84·9 (1)°]. The range of W···Cu distances, bridged by μ_3-S^{2-} ligands, is 2·632 (1)–2·675 (1) Å.

Experimental. Compound prepared from [PhP]$_2$[WS$_4$] and CuCl (1:4) in acetone at room temperature, red crystals obtained by slow evaporation of the solvent. Crystal size 0·23 × 0·37 × 0·37 mm, Siemens AED2 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values of 32 reflections measured at $\pm\omega$ (20 < 2θ < 22°). Intensity measurements in ω/θ scan mode, scan width =

1·02° + α-doublet separation, scan time = 14–56 s, $2\theta_{max} = 50°$, h −15→0, k −17→17, l −18→18, no significant variation in intensity for three standard reflections, semi-empirical absorption correction (transmission 0·282–0·424). 9322 reflections, 9011 unique ($R_{int} = 0\cdot019$), 7180 with $F > 4\sigma(F)$ for structure solution (by Patterson and difference syntheses) and refinement (blocked-cascade least squares on F), $w^{-1} = \sigma^2(F) + 0\cdot00004F^2$. Anisotropic thermal parameters for all non-H atoms, H atoms constrained [C–H = 0·96 Å on ring-angle external bisectors, U(H) = $1\cdot2U_{eq}$(C)], isotropic extinction parameter $x = 5\cdot6$ (2) × 10^{-7} [$F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{1/4}$], 569 parameters, max. $\Delta/\sigma = 0\cdot084$, mean $= 0\cdot021$, $R = 0\cdot033$, $wR = 0\cdot035$, slope of normal probability plot $= 1\cdot48$, max. $\Delta\rho = +0\cdot77$ e Å^{-3}, min. $= -0\cdot77$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974), *SHELXTL* programs (Sheldrick, 1985).

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,† selected bond lengths and angles for the anion in Table 2. The atom-numbering scheme for the dimeric anion is shown in Fig. 1.

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43565 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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* IUPAC name: tetrakis(tetraphenylphosphonium) 1,1'-di-μ-chloro-bis{[2,3,4-trichloro-1,2;2,3;3,4;4,1-tetra-μ-thio-tetracuprato-(I)-S^1,S^2,S^3,S^4]tungstate}(4−).