Mercury(II) Halide Complexes of Tertiary Phosphines. Part 9.† Study of the Tris(2-cyanoethyl)phosphine Complexes $[HgX_2\{P(CH_2CH_2CN)_3\}_m]$ (X = Cl, Br, or I; m = 1 or 2): Crystal Structures of $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ and $[\{HgCl_2[P(CH_2CH_2CN)_3]\}_n]$ ‡

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The complexes $[HgX_2\{P(CH_2CH_2CN)_3\}_m]$ (X = Cl, Br, or I; m = 1 or 2) have been prepared and characterised by analytical and far-i.r. spectroscopic data. In addition, the *X*-ray crystal structures of $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ (1) and $[\{HgCl_2[P(CH_2CH_2CN)_3]\}_n]$ (2) have been determined. Crystals of (1) are monoclinic, space group $P2_1/n$, with a = 9.174(6), b = 15.795(9), c = 20.741(11) Å, β = 93.01(5)°, and Z = 4; those of (2) are orthorhombic, space group $P2_12_12_1$, with a = 20.872(14), b = 7.854(8), c = 8.519(9) Å, and Z = 4. Both structures were solved using the heavy-atom method and refined to final R values of 0.043 for (1) and 0.053 for (2) using 2 511 and 1 252 observed diffractometer data respectively. Complex (1) is found to be monomeric, while (2) adopts a polymeric structure in which almost linear $Cl-Hg-P(CH_2CH_2CN)_3$ units are linked by chlorine atoms to give single chains. The geometry about mercury in the two complexes indicates tris(2-cyanoethyl)phosphine to be a strong σ-donor and comparable with triethylphosphine in its interactions with mercury(II) halides. This is confirmed by far-i.r. studies of the six complexes prepared.

In our study of complexes formed between tertiary phosphines and mercury(II) halides, we have shown [1-8] that structural variations in the complexes $[HgX_2(PR_3)_m]$ (m = 1 or 2) can be rationalised in terms of the varying σ-donor strengths of the PR_3 ligands coupled with the tendency for mercury(II) towards linear co-ordination. While electronic factors appear to be dominant in determining the solid-state structure adopted by these complexes, steric factors cannot be discounted, and indeed Mason and Meek [9] consider the difference between steric and electronic effects involving tertiary phosphines to be 'semantic'. In order to clarify the relative importance of steric and electronic factors, we have examined the co-ordination characteristics of tris(2-cyanoethyl)phosphine, which is expected to have similar steric requirements to triethylphosphine (particularly in the region of co-ordination), but has a markedly lower basicity (pK_a = 1.37) [10] than triethylphosphine or other common tertiary phosphines. The complexes $[HgX_2\{P(CH_2CH_2CN)_3\}_m]$ (X = Cl, Br, or I; m = 1 or 2) have been prepared and characterised by analytical and far-i.r. spectroscopic data (see Experimental section). In addition, single-crystal *X*-ray analyses of $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ (1) and $[\{HgCl_2[P(CH_2CH_2CN)_3]\}_n]$ (2) have been conducted.

Results and Discussion

All the compounds studied were recrystallised from acetone as solvent-free compounds except $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]$ which recrystallised with one mole of solvent per formula unit and the corresponding iodide which on recrystallisation yielded either the 1 : 1 complex (using acetone or ethanol as solvent) or ill-defined products (using $CHCl_3$ or CH_2Cl_2).

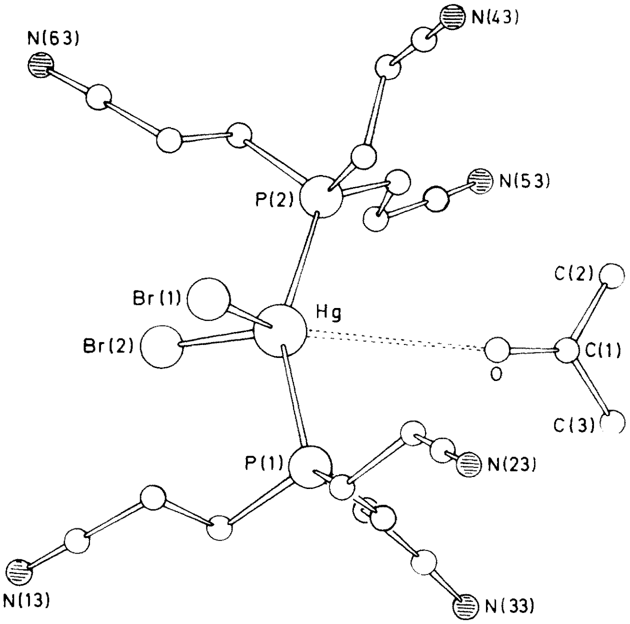

Figure 1. Molecular structure of $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ (1)

The complex $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ (1) is found to be monomeric in the solid state (Figure 1) and selected bond distances and angles are given in Table 1. The most noteworthy feature of the geometry about mercury is the very large P–Hg–P angle of 151.3(1)° which is comparable with the value of 158.5(5)° found in $[HgCl_2(PEt_3)_2]$ [3] and substantially larger than that in $[HgBr_2(PPh_3)_2]$ [113.0(5)°].[8] The acetone of crystallisation is situated such that the oxygen atom occupies an equatorial position of a trigonal bipyramidal polyhedron about mercury. However, the extreme length of the Hg···O distance [3.91(2) Å], which is significantly greater than the sum of the van der Waals radii (3.25 Å),[11] indicates the interaction to be extremely weak. On the other hand, the i.r. spectrum shows ν(CO) at 1 701 cm^{-1}, a shift

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† Part 8, N. A. Bell, M. Goldstein, L. A. March, and I. W. Nowell, *Inorg. Chim. Acta*, 1984, **83**, 75.

‡ Dibromobis[tris(2-cyanoethyl)phosphine]mercury(II)-acetone (1/1) and *catena*-μ-chloro-chloro[tris(2-cyanoethyl)phosphine]-mercury(II) respectively.

Supplementary data available (No. SUP 23938, 24 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Selected bond lengths (Å) and angles (°) for [HgBr$_2${P(CH$_2$CH$_2$CN)$_3$}$_2$]·Me$_2$CO (1) and [{HgCl$_2$[P(CH$_2$CH$_2$CN)$_3$]}$_n$] (2) *

(*a*) Bond lengths

Complex (1)		Complex (2)	
Hg–Br(1)	2.750(2)	Hg–Cl(1)	2.780(7)
Hg–Br(2)	2.703(2)	Hg–Cl(1′)	2.714(7)
Hg–P(1)	2.441(3)	Hg–Cl(2)	2.331(7)
Hg–P(2)	2.440(3)	Hg–P	2.393(5)
Hg · · · O	3.91(2)	Hg · · · C(23)	3.41(3)
		Hg · · · N(23)	3.58(3)
		Hg · · · C(23‴)	3.65(3)
		Hg · · · N(23‴)	3.47(3)

(*b*) Bond angles

Complex (1)		Complex (2)	
Br(1)–Hg–Br(2)	107.3(1)	Cl(1)–Hg–Cl(1′)	98.8(3)
Br(1)–Hg–P(1)	97.2(1)	Cl(1)–Hg–Cl(2)	99.0(3)
Br(1)–Hg–P(2)	95.2(1)	Cl(1)–Hg–P	90.2(2)
Br(1)–Hg–O	137(1)	Cl(1′)–Hg–Cl(2)	98.1(3)
Br(2)–Hg–P(1)	99.3(1)	Cl(1′)–Hg–P	95.8(2)
Br(2)–Hg–P(2)	101.5(1)	Cl(2)–Hg–P	162.0(3)
Br(2)–Hg–O	116(1)	Hg–Cl(1)–Hg″	142.7(2)
P(1)–Hg–P(2)	151.3(1)		
P(1)–Hg–O	78(1)		
P(2)–Hg–O	75(1)		

* Symmetry operations: one prime, $-x$, $-0.5 + y$, $-0.5 - z$; two primes, $-x$, $-0.5 + y$, $0.5 - z$; three primes, $-x$, $0.5 + y$, $0.5 - z$.

Table 2. Comparison of Hg–ligand distances (Å) in [HgBr$_2${P(CH$_2$CH$_2$CN)$_3$}$_2$]·Me$_2$CO (1) and [HgBr$_2$(PPh$_3$)$_2$] [8]

	Complex (1)	[HgBr$_2$(PPh$_3$)$_2$]
Hg–Br	2.703(2), 2.750(2)	2.626(8), 2.633(6)
Hg–P	2.440(3), 2.441(3)	2.535(15), 2.540(16)

Table 3. Spectroscopic data for [HgX$_2$L$_m$] [X = Cl, Br, or I; L = P(CH$_2$CH$_2$CN)$_3$; m = 1 or 2]

Complex	ν(CN)/ cm^{-1}	ν(HgX)$_t$ [a]/ cm^{-1}	ν(HgX)$_b$ [b]/ cm^{-1}
(2) [{HgCl$_2$L}$_n$]	2 247	323	195
[HgBr$_2$L]	2 253	205	*c*
[HgI$_2$L]	2 250	177	*c*
[HgCl$_2$L$_2$]	2 246	207, 188	—
(1) [HgBr$_2$L$_2$]·Me$_2$CO [d]	2 249	135br	—
[HgI$_2$L$_2$]	2 244	123, 109	

[a] t = terminal. [b] b = bridging. [c] There are several strong candidate bands in the region below 150 cm^{-1}, but no individual assignment is justified. [d] ν(CO) at 1 701 cm^{-1}.

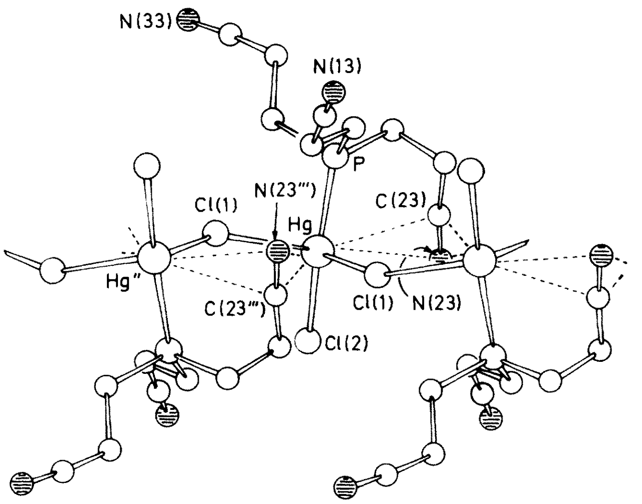

Figure 2. Polymeric structure of [{HgCl$_2$[P(CH$_2$CH$_2$CN)$_3$]}$_n$] (2), showing part of the chain running parallel to *b*. For clarity, hydrogen atoms have been omitted

from that in liquid acetone (*ca.* 20 cm^{-1}) which is by no means insignificant and which cannot be attributed simply to dispersion forces. Thermal studies also support the presence of quite a strong interaction between the acetone and mercury. Mass loss (6.8%) corresponding to evolution of acetone (required 7.1%) occurred over the range 90—100 °C with a relatively high desolvation endotherm (150 ± 6 kJ mol^{-1}) at 101 °C, followed by a melting endotherm (38 ± 3 kJ mol^{-1}) at 187 °C (visual m.p. 178—179 °C). Mass losses over the range 210—350 °C approximated to the loss of ligand as an exothermic process (311 ± 2 kJ mol^{-1}) at 346 °C and over the range 350—950 °C to loss of HgBr$_2$ as an endotherm (82 ± 9 kJ mol^{-1}) at 461 °C, but the decomposition was complicated, probably by oxidation of ligand, so that a residue of 11% remained even at 950 °C.

It is therefore likely that the presence of the acetone molecule within the co-ordination sphere of the mercury atom makes some contribution to the enlarged P–Hg–P angle, but the crystallographic data show quite clearly that strong interaction between the two phosphine ligands and the metal is also a substantive cause. Thus comparison of the mercury-ligand distances in (1) with those in [HgBr$_2$(PPh$_3$)$_2$] (Table 2) shows the Hg–Br bonds in the present complex to be substantially longer while the Hg–P bonds are significantly shorter. This is exactly the behaviour expected for tris(2-cyanoethyl)phosphine to be a strong σ-donor.[3]

Verification that the strong σ-donor ability of the tris(2-cyanoethyl)phosphine is *itself* sufficient to account for the large P–Hg–P angles observed comes from a study of the far-i.r. spectra. In the spectra of all three 2 : 1 complexes, the ν(HgX) band positions (Table 3) are in the same regions as found for PEt$_3$ and PBu$_3$ analogues, and substantially lower than found in [HgX$_2$(PPh$_3$)$_2$].[3] Since the chloride and iodide 2 : 1 complexes presently studied contain no acetone of crystallisation, it is plain that tris(2-cyanoethyl)phosphine acts as a strong σ-donor towards mercury(II), comparable to PEt$_3$ and PBu$_3$.

The complex [{HgCl$_2$[P(CH$_2$CH$_2$CN)$_3$]}$_n$] (2) is found to be polymeric with almost linear Cl–Hg–P(CH$_2$CH$_2$CN)$_3$ units bridged by further chlorine atoms (Figure 2). The resulting arrangement, in which single chains run parallel to the *b* axis, is quite different to the associated structures found in [{HgCl$_2$(PR$_3$)}$_n$] (R = Me or Et).[1-4] It is surprising that the polymeric arrangement in (2) is so different to that in the triethylphosphine complex, but closer examination of the orientation of the cyanoethyl groups affords a possible explanation. In contrast to the P–C–C–CN torsion angles found for two of the cyanoethyl groups, which lie close to the expected value of 180° and to the values in (1) (170—171°), that of P–C(21)–C(22)–C(23) is only 75°. While such an arrangement may be energetically less favourable than the *trans* conformation in the other cyanoethyl groups, it does allow C(23)N(23) and the symmetry related C(23‴)N(23‴) group to take up positions close to the mercury atom. The resulting Hg–C(23),N(23) distances (Table 1) are longer than the sum of the van der Waals radii (3.40, 3.30 Å respectively)[11]

Table 4. Melting points and analytical data for $[HgX_2L_m]$ [X = Cl, Br, or I; L = $P(CH_2CH_2CN)_3$; m = 1 or 2] with calculated values in parentheses

Complex	C (%)	H (%)	N (%)	M.p. (°C)
(2) $[\{HgCl_2L\}_n]$	23.30	2.55	8.85	215—216
	(23.40)	(2.60)	(9.00)	
$[HgBr_2L]$	19.50	2.05	7.40	184—185
	(19.55)	(2.20)	(7.60)	
$[HgI_2L]$	16.60	1.70	6.35	235—236
	(16.70)	(1.85)	(6.50)	
$[HgCl_2L_2]$	32.95	3.60	12.75	160—162
	(32.85)	(3.65)	(12.80)	
(1) $[HgBr_2L_2]\cdot Me_2CO$	31.35	3.75	10.35	178—179
	(31.35)	(3.75)	(10.45)	
$[HgI_2L_2]$	25.85	2.80	9.85	160—163
	(25.70)	(2.85)	(10.00)	

indicating that the π-interaction is weak. This is also shown in the i.r. spectrum, where the ν(CN) band, although at a marginally lower wavenumber than in the other 1 : 1 complexes (Table 3), does not show any sign at all of the splitting expected from the presence of both co-ordinated and unco-ordinated cyano-groups. Even under high resolution conditions, the ν(CN) band appeared remarkably sharp and symmetrical. On the other hand, the π-interaction of the cyano-groups with mercury is nevertheless of sufficient importance to prevent formation of the polymeric arrangement found in $[\{HgCl_2(PEt_3)\}_n]$ in which both chlorine atoms are involved in bridging. The C(23)N(23) groupings in (2) could be considered to be functioning as bridging ligands, weakly interacting with adjacent metal centres (Figure 2).

The resulting co-ordination polyhedron about mercury is best described as distorted octahedral, with the two cyano-groups being *trans* to each other. The P–Hg–Cl(2) angle of 162.0(3)° is almost identical to that found in $[\{HgCl_2(PMe_3)\}_n]$ [162.1(1)°] and is further evidence that tris(2-cyanoethyl)-phosphine functions as a strong σ-donor in these mercury(II) halide complexes. In keeping with this, the Hg–P and Hg–Cl(2) distances are particularly short, and are comparable with those in the trimethylphosphine complex. The shortness of the Hg–Cl(2) bond is clearly reflected in the far-i.r. spectrum, where $\nu(HgCl)_t$ at 323 cm^{-1} (Table 3) is more than 20 cm^{-1} to higher wavenumber than for any other known $[HgX_2(PR_3)]$ complex.[7,12] An analogous situation pertains for $[HgI_2\{P(CH_2CH_2CN)_3\}]$, while ν(HgBr) for the analogous bromide, although not at the highest wavenumber is at the upper end of the range established.

We thus conclude that for both series of complexes studied the geometry about mercury shows tris(2-cyanoethylphosphine) to be a strong σ-donor ligand with a donor strength comparable to that of triethylphosphine. The electron-withdrawing property of the cyano-groups, while significantly lowering the pK_a of tris(2-cyanoethyl)phosphine compared to that of triethylphosphine does not appear to significantly reduce the co-ordinating ability of the substituted phosphine in its interaction with mercury(II) halides.

Experimental

(i) *Preparation and Analysis of the Complexes.*—The complexes were prepared by mixing the ligand and the mercury(II) halide in the appropriate mol ratio, both dissolved in the minimum of warm ethanol. The resulting white precipitates were filtered off and, except for $[HgI_2\{P(CH_2CH_2CN)_3\}_2]$, were recrystallised from acetone and finally dried *in vacuo*. Analytical (C, H, and N) and melting point data are reported in Table 4.

Table 5. Final fractional co-ordinates (Hg × 10^5; other atoms × 10^4) with estimated standard deviations in parentheses

(*a*) $[HgBr_2\{P(CH_2CH_2CN)_3\}_2]\cdot Me_2CO$ (1)

Atom	*x*	*y*	*z*
Hg	26 835(7)	12 825(4)	26 700(2)
Br(1)	5 682(2)	1 215(1)	2 708(1)
Br(2)	1 913(4)	2 934(1)	2 618(1)
P(1)	2 393(4)	1 019(2)	3 816(1)
P(2)	2 351(4)	870(2)	1 538(1)
C(11)	2 793(18)	1 971(8)	4 291(6)
C(12)	4 291(23)	2 310(10)	4 166(8)
C(13)	4 628(21)	3 107(9)	4 503(7)
N(13)	4 822(19)	3 735(10)	4 745(7)
C(21)	3 661(19)	245(9)	4 141(6)
C(22)	3 604(24)	−585(9)	3 747(9)
C(23)	4 521(21)	−1 225(10)	4 034(7)
N(23)	5 222(22)	−1 738(9)	4 254(7)
C(31)	623(18)	685(10)	4 069(7)
C(32)	−647(19)	1 270(14)	3 853(8)
C(33)	−1 919(23)	968(15)	4 167(8)
N(33)	−2 885(25)	764(19)	4 460(10)
C(41)	3 574(18)	7(8)	1 381(6)
C(42)	3 589(23)	−275(12)	665(7)
C(43)	4 545(27)	−998(11)	582(8)
N(43)	5 286(27)	−1 571(12)	514(9)
C(51)	551(17)	519(9)	1 258(6)
C(52)	−622(18)	1 148(10)	1 426(7)
C(53)	−2 048(22)	869(12)	1 132(8)
N(53)	−3 108(19)	645(12)	891(8)
C(61)	2 789(17)	1 742(8)	1 002(6)
C(62)	4 282(21)	2 120(11)	1 171(9)
C(63)	4 561(24)	2 874(10)	790(9)
N(63)	4 820(27)	3 471(11)	514(9)
O	−556(28)	−332(15)	2 626(9)
C(1)	−1 536(39)	−882(17)	2 559(13)
C(2)	−1 880(45)	−1 310(20)	1 923(13)
C(3)	−2 469(38)	−1 141(26)	3 087(14)

(*b*) $[\{HgCl_2[P(CH_2CH_2CN)_3]\}_n]$ (2)

Atom	*x*	*y*	*z*
Hg	−514(3)	14 482(13)	−4 987(11)
Cl(1)	190(3)	4 620(8)	−1 820(8)
Cl(2)	−1 134(3)	1 802(16)	91(13)
P	1 075(2)	960(7)	−232(7)
C(11)	1 451(11)	455(34)	−2 087(26)
C(12)	1 332(11)	1 711(35)	−3 454(29)
C(13)	1 730(12)	1 331(39)	−4 723(23)
N(13)	2 075(12)	1 068(33)	−5 728(29)
C(21)	1 275(11)	−733(40)	1 044(32)
C(22)	930(14)	−2 433(39)	783(28)
C(23)	219(16)	−2 315(39)	1 384(45)
N(23)	−261(14)	−2 440(64)	1 628(38)
C(31)	1 448(9)	2 907(32)	563(30)
C(32)	2 170(10)	2 888(34)	758(25)
C(33)	2 364(15)	4 393(48)	1 607(33)
N(33)	2 513(15)	5 588(55)	2 190(46)

(ii) *Thermal Analysis.*—A Stanton-Redcroft TG 750 thermobalance and differential thermogravimetric (d.t.g.) unit, together with open Pt crucibles were used for the thermogravimetric study. The sample (7.5 mg) was heated at 10 °C min^{-1} in a dynamic atmosphere of column-dried air (5 cm^3 min^{-1}). Quantitative d.t.a. data were obtained using a Stanton-Redcroft 673/4 instrument with quartz crucibles. Samples (9.5 and 12.0 mg) were heated at 20 °C min^{-1} in a quartz crucible under a dynamic atmosphere of nitrogen (200 cm^3

min^{-1}) using Al_2O_3 as reference. Reaction enthalpies (ΔH_R/kJ mol^{-1}) have been derived from the peak areas of the melting and decomposition endotherms by means of the expression: $\Delta H_R = 10^3\ AM/Km$, where A is the peak area (mm^2), M is the molar mass of the complex, K is a calibration constant ($\text{mm}^2\ \text{mJ}^{-1}$) for a given reaction temperature (T/°C), and m is the sample mass (mg).

(iii) *Infrared Spectra.*—Infrared spectra in the range 4 000—600 cm^{-1} were recorded as Nujol mulls using a Perkin-Elmer 557 i.r. spectrophotometer. Far-i.r. spectra (400—50 cm^{-1}) were obtained as described previously,[7] with the samples prepared as Nujol mulls between polyethene windows.

Crystallographic Studies.—Crystals suitable for *X*-ray work were mounted with a unit-cell axis [(1), *a*; (2), *c*] coincident with the ω-axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using the background-ω-scan background technique and with graphite monochromated Mo-K_α radiation. Data were corrected for Lorentz, polarisation, and absorption effects and 2 511 [for (1)] and 1 252 [for (2)] unique reflections having $I/\sigma(I) > 3.0$ were used for subsequent analysis. The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. Hydrogen atoms were included in ideal positions (C–H, 1.08 Å) and given a common isotropic temperature factor, while all other atoms were assigned anisotropic thermal parameters. Complex neutral-atom scattering factors [13] were employed throughout the refinement and a non-unit weighting scheme of the form $w = a/[\sigma^2(F_o) + b(F_o)^2]$ was adopted in the final stages of the refinement [final values of *a*, *b*: 1.0000, 0.0040, (1); 0.0356, 0.1967, (2)]. The final *R* values for (1) [and (2)] were $R = 0.043$ (0.053) and $R' = 0.045$ (0.060) respectively. [Attempts to change the handedness in (2) led to a higher *R* value, 0.063, and less satisfactory refinement of the anisotropic temperature factors.] All calculations were performed on an IBM 4341 computer using SHELX.[14]

Crystal data. Complex (1). $C_{21}H_{30}Br_2HgN_6OP_2$, $M = 821.1$, monoclinic, $a = 9.174(6)$, $b = 15.795(9)$, $c = 20.741(11)$ Å, $\beta = 93.01(5)°$, $U = 3\,001.4$ Å^3, $F(000) = 1\,544$, space group $P2_1/n$, $D_m = 1.84$, $Z = 4$, $D_c = 1.82$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) 76.6 cm^{-1}.

Complex (2). $C_9H_{12}Cl_2HgN_3P$, $M = 472.8$, orthorhombic, $a = 20.872(14)$, $b = 7.854(8)$, $c = 8.519(9)$ Å, $U = 1\,396.4$ Å^3, $F(000) = 864$, space group $P2_12_12_1$, $D_m = 2.23$, $Z = 4$, $D_c = 2.25$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) 110.6 cm^{-1}.

Table 5 lists the final atomic parameters.

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