

Two phases of $\{[\text{CsPH}(\eta^6\text{-}2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}\}_x$: their structures and interconversions

Thomas E. Concolino,^a
Kin-Chung Lam,^a Ilia A. Guzei,^a
Arnold L. Rheingold^{a*} and
Gerd W. Rabe^b

^aDepartment of Chemistry and Biochemistry,
University of Delaware, Newark, DE 19716,
USA, and ^bAnorganisch-chemisches Institut,
Technische Universität München, Lichtenberg-
strasse 4, 85747 Garching, Germany

Correspondence e-mail: arnrhein@udel.edu

The solvent-bridged caesium phosphide $\{[\text{CsPH}(\eta^6\text{-}2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}\}_x$, *catena*- $[(\mu\text{-}\eta^3\text{-toluene})\text{-bis}[\text{caesium}(2,4,6\text{-tri-}t\text{-butylphenylphosphide})]]$, undergoes a reversible solid-state, order–disorder phase transition characterized by the doubling of the unit-cell volume at low temperature achieved by doubling one unit-cell vector. The unit-cell parameters at 293 (2) K (form *A*) are: $a = 11.147$ (4), $b = 14.615$ (4), $c = 14.806$ (5) Å, $\alpha = 70.57$ (3), $\beta = 71.85$ (3), $\gamma = 72.93$ (2)°, $V = 2112.5$ (12) Å³, $Z = 2$, $\rho_{\text{calc}} = 1.362$ g cm⁻³, $R_1 = 0.0513$ for 5462 reflections, $wR_2 = 0.0947$ for all data. The unit-cell parameters at 173 (2) K (form *B*) are: $a = 14.6241$ (3), $b = 14.7393$ (3), $c = 22.0720$ (4) Å, $\alpha = 72.2117$ (7), $\beta = 73.3659$ (8), $\gamma = 70.2953$ (7)°, $V = 4174.8$ (2) Å³, $Z = 4$, $\rho_{\text{calc}} = 1.379$ g cm⁻³, $R_1 = 0.0405$ for 14 010 reflections, $wR_2 = 0.1326$ for all data. With a minor change, the key structural features discussed previously for form *A* [Rabe *et al.* (1998). *Inorg. Chem.* **37**, 4235–4245] remain unchanged. The η^3 -toluene ligand is observed to be disordered at 293 (2) K and ordered at 173 (2) K, with the order–disorder phase transition occurring at approximately 278 (2) K.

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1. Introduction

Many compounds have been observed *via* crystallographic studies to undergo solid–solid phase transformations on cooling (see Wang, 1979; Sarma & Dunitz, 1990; Richardson *et al.*, 1990; Hsu & Nordman, 1983). Dunitz has studied a series of polymorphs of *p*-(trimethylammonio)benzenesulfonate (see Sarma & Dunitz, 1990) and 3,6-dichloro-2,5-dihydroxyterephthalate (see Richardson *et al.*, 1990). In these cases, it has been a change in the systematic absences and/or crystal structure that resulted in the discovery of the new polymorph. However, the present caesium phosphide, $\{[\text{CsPH}(\eta^6\text{-}2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}\}_x$, is characterized by only an axis doubling, a phenomenon for which we could find only two previous examples, neither of which could be fully investigated. A study by Farrugia *et al.* (1996) reports on the phase transition of Fe₂Os(CO)₁₂ on heating to 373 K leading to an axis halving, but crystal decomposition did not allow a data collection to be performed.

In a study by Churchill & Chang (1974) on the complex $[(\text{Me}_6\text{C}_6)_3\text{Nb}_3\text{Cl}_6][\text{Cl}]$, axial photos revealed a set of diffuse reflections at intermediate spacings along the *c* axis. It was suggested that there could be a poorly defined superlattice. It would be of interest to re-examine this species at a variety of temperatures to determine if the intensity of these reflections increases to yield a volume-doubled species.

The idea of order–disorder phase transitions is not new (Dornberger-Schiff, 1956), with several articles being published on the subject (for a review on dynamic processes in

Table 1
Experimental details.

	(1A)	(1B)
Crystal data		
Chemical formula	$[[\text{Cs}(\text{C}_{18}\text{H}_{30}\text{P})]_2 \cdot 0.5(\text{C}_7\text{H}_8)]_x$	$[[\text{Cs}(\text{C}_{18}\text{H}_{30}\text{P})]_2 \cdot 0.5(\text{C}_7\text{H}_8)]_x$
Chemical formula weight	866.16	866.67
Cell setting	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	11.147 (4)	14.6241 (3)
<i>b</i> (Å)	14.615 (4)	14.7393 (3)
<i>c</i> (Å)	14.806 (5)	22.0720 (4)
α (°)	70.57 (3)	72.2117 (7)
β (°)	71.85 (3)	73.3659 (8)
γ (°)	72.93 (2)	70.2953 (7)
<i>V</i> (Å ³)	2112.5 (12)	4174.8 (2)
<i>Z</i>	2	4
<i>D_x</i> (Mg m ⁻³)	1.362	1.379
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	34	8192
θ range (°)	7.5–12.5	2.0–25.0
μ (mm ⁻¹)	1.825	1.847
Temperature (K)	293 (2)	173 (2)
Crystal form	Rod	Block
Crystal size (mm)	0.30 × 0.15 × 0.15	0.25 × 0.25 × 0.20
Crystal colour	Yellow	Yellow
Data collection		
Diffractometer	Siemens P4	Siemens P4/CCD area detector
Data collection method	ω scans	φ and ω scans
Absorption correction	ψ	Empirical
<i>T</i> _{min}	0.450	0.6553
<i>T</i> _{max}	0.586	0.7090
No. of measured reflections	6485	25526
No. of independent reflections	5462	14010
No. of observed reflections	3175	12235
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	0.038	0.042
θ _{max} (°)	22.50	25.00
Range of <i>h, k, l</i>	−1 → <i>h</i> → 11 −14 → <i>k</i> → 15 −15 → <i>l</i> → 15	−17 → <i>h</i> → 17 −16 → <i>k</i> → 17 −26 → <i>l</i> → 24
No. of standard reflections	3	–
Frequency of standard reflections	Every 197 reflections	–
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$	0.051	0.041
$wR(F^2)$	0.095	0.149
<i>S</i>	1.148	1.173
No. of reflections used in refinement	5462	14010
No. of parameters used	405	800
H-atom treatment	Idealized contributions	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.029	0.002
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.49	0.70
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	−0.86	−0.83
Extinction method	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	<i>XSCANS</i> (Siemens, 1994)	<i>SMART</i> (Siemens, 1995)
Cell refinement	<i>XSCANS</i> (Siemens, 1994)	<i>SMART</i> (Siemens, 1995)
Data reduction	<i>XSCANS</i> (Siemens, 1994)	<i>SHELXTL97</i> (Sheldrick, 1997 <i>b</i>)
Structure solution	<i>SHELXL</i> (Sheldrick, 1994)	<i>SHELXS97</i> (Sheldrick, 1990)
Structure refinement	<i>SHELXL</i> (Sheldrick, 1994)	<i>SHELXL97</i> (Sheldrick, 1997 <i>a</i>)
Preparation of material for publication	<i>XCIF</i> (Sheldrick, 1994)	<i>SHELXTL97</i> (Sheldrick, 1997 <i>b</i>)

crystalline organometallic complexes see Braga, 1992). Fe₂Os(CO)₁₂ has been studied by Churchill & Fettinger (1990) and Farrugia *et al.* (1996). In the first study the data collection was performed at 297 K, yielding a structure with 12:1 disorder in the metal-atom positions. In the latter study, data collections were performed at 120, 223, 288, 292 and 323 K on the same crystal. The study revealed that at 120 and 223 K no disorder of the metal positions was evident. However, at 323 K, disordered metal-atom positions at a ratio of 1.4:1 were found. The variable-temperature studies were performed on the same crystal demonstrating that it was a dynamic process in the solid state that led to the disorder.

They further examined the process by ¹³C MAS NMR and proved that the disorder occurred *via* an in-plane rotation of the metal-atom core. However, these results occurred without a change in the unit-cell dimensions. Attempts to perform a data collection at 373 K yielded a unit cell with a halving of the *b* axis, suggesting that the crystal became completely disordered, giving a structure similar to the previously reported structure of Fe₃(CO)₁₂, see Wei & Dahl (1969), Cotton & Troup (1974) and Braga *et al.* (1994). However, as mentioned earlier, extensive crystal decomposition at that temperature did not permit a data collection.

Further studies on both Fe₂Ru(CO)₁₂ and FeRu₂(CO)₁₂ revealed that as the temperature of the system was raised above 313 and 228 K, respectively, an axis vector was halved. This increase in the symmetry of the observed space groups manifested itself in the increased disorder of the FeRu triangle (Braga *et al.*, 1996).

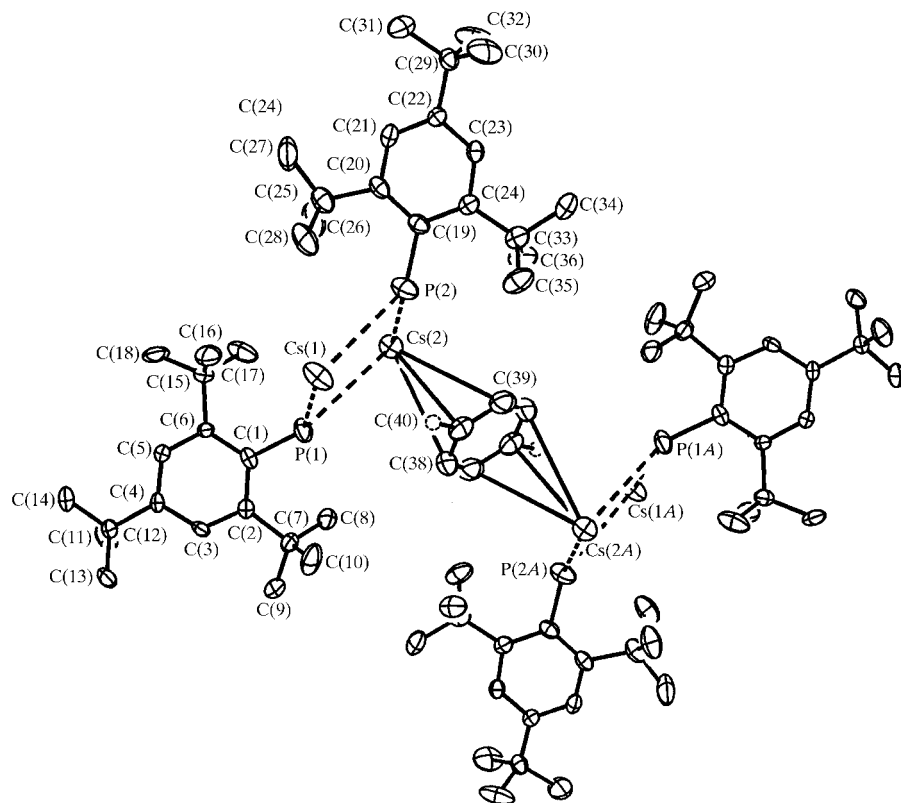


Figure 1
ORTEP (Johnson, 1965) drawing of form (1A) with thermal ellipsoids drawn at 30% probability and H atoms omitted for clarity.

We previously reported the structure of $\{[\text{CsPH}(\eta^6\text{-}2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}\}_x$ (1) at 293 (2) K by Rabe *et al.* (1998). A second data collection was performed at 173 (2) K. As the crystal was cooled below 278 (2) K, the length of the *a* axis doubled. In this case the compound has undergone a rapid solid-state change (within 20 min the transformation is complete), causing previously unobserved reflections to be observed, resulting in the doubling of the unit-cell volume.

2. Crystal structural determination

Crystal, data collection and refinement parameters are given in Table 1.¹ All crystals were mounted in glass capillaries in a drybox under a nitrogen atmosphere. The data collection for (1A) (Fig. 1) was performed on a Siemens P4 diffractometer equipped with a scintillation detector at 293 K, as previously reported (Rabe *et al.*, 1998). A second data collection was performed on a second crystal at 173 K on a Siemens P4 instrument equipped with a SMART/CCD detector resulting in form (1B) (Fig. 2).

Both samples crystallized in the triclinic space group $P\bar{1}$. Comparison of the unit-cell indices indicates that a doubling of the *a* axis of form A occurs. A third sample was mounted to determine if the process was reversible. A hemispherical

matrix determination was performed at room temperature on the crystal using the Siemens P4 diffractometer, giving the unit-cell indices corresponding to form (1A). The crystal was then cooled to 233 K and the volume-doubled unit-cell indices of form (1B) were observed. The temperature of the crystal was then raised in 5 K increments and allowed to equilibrate for 20 min prior to the matrix determination. Upon equilibration, a hemispherical matrix determination was performed to determine the temperature at which the transition from the small unit cell to the volume-doubled unit cell occurs [approximately 278 (2) K]. Axial photos were taken at each temperature.

A fourth, much larger, crystal with dimensions of approximately $0.8 \times 0.6 \times 0.4$ mm was mounted to examine whether the phenomenon was simply a weakening of the intensity of the reflections necessary to yield the volume-doubled unit cell. A matrix determination was performed on this crystal at room temperature. The smaller unit-cell indices were again found. Axial photos, taken for five times

longer than the previous photos, revealed that it was not a weakening of the intensity of the reflections, but a true solid-state transformation.

3. Structural details

The structure of $\{[\text{CsPH}(\eta^6\text{-}2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}\}_x$ (1) exists as four-rung ladder frameworks bridged by mutually η^3 -toluene molecules. The ladder segments are stacked as parallel layers, as shown in Figs. 3 and 4. There are two different Cs-atom coordination environments. In form (1A), Cs(1) is bonded to three phosphide ligands and in contact with two Cs atoms; in form (1B), Cs(1) and Cs(3) are in this mode. The second coordination environment observed is when a Cs atom is bonded to two phosphide ligands and in contact with

Table 2
Important bond lengths (Å) and angles (°).

	(1A)	(1B)
Cs(2)—Cs(2) ⁱ	5.564 (3)	5.4810 (6)
Cs(1)—Cs(2)		5.4902 (4)
Cs(1)—Cs(1) ⁱⁱ	4.787 (2)	
Cs(1)—Cs(3) ⁱⁱⁱ		4.7772 (4)
P(2)—Cs(1)—P(1) ⁱⁱ	165.49 (8)	
P(1)—Cs(1)—P(3) ⁱⁱ		161.70 (3)
P(1)—Cs(2)—Cs(2) ⁱ	128.65 (6)	
P(2)—Cs(2)—Cs(2) ⁱ		131.30 (2)

Symmetry transformations used to generate equivalent atoms: form (1A): (i) $-x - 1, -y + 3, -z + 1$; (ii) $-x, -y + 2, -z + 1$; form (1B): (i) $-x + 1, -y + 2, -z$; (ii) $x + 1, y, z$.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS0009). Services for accessing these data are described at the back of the journal.

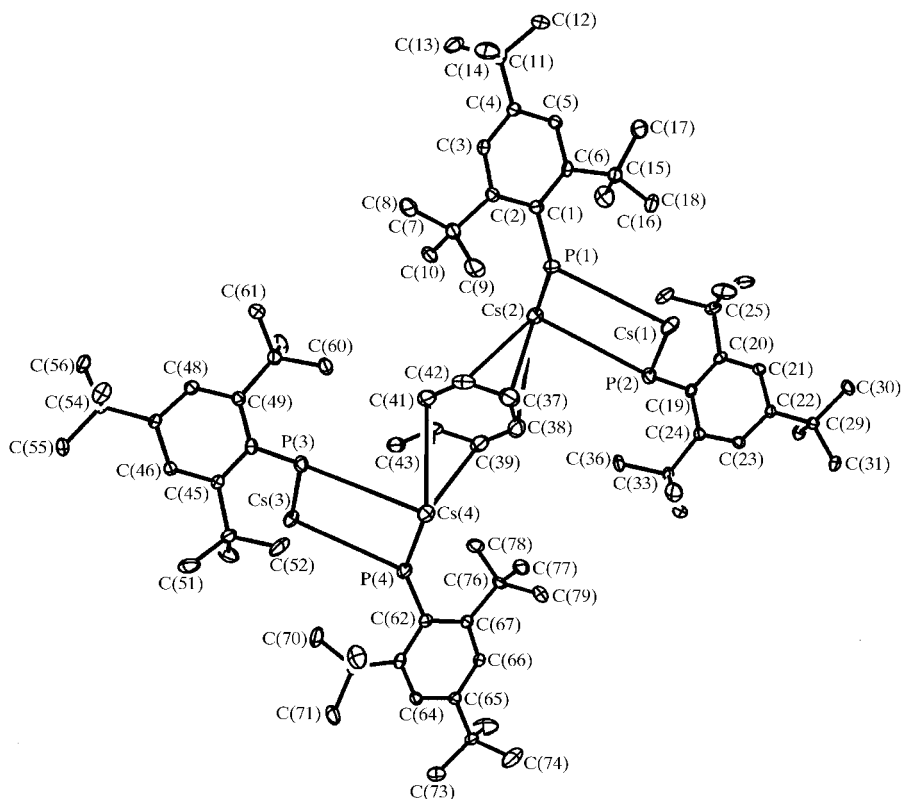


Figure 2
ORTEP (Johnson, 1965) drawing of form (1B) with thermal ellipsoids drawn at 30% probability and H atoms omitted for clarity.

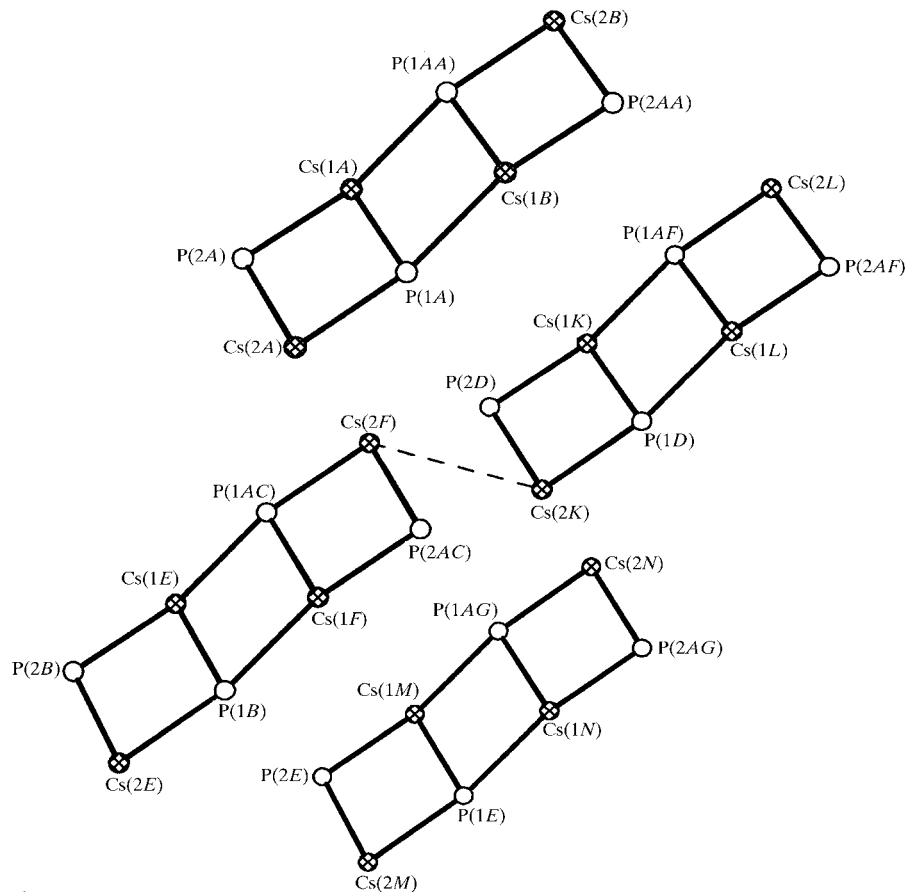


Figure 3
Ball-and-stick drawing of the Cs–P framework of (1A), as viewed down the *b* axis.

one Cs atom, and is further coordinated to the bridging toluene ligand, Cs(2) in form (1A), and Cs(2) and Cs(4) in form (1B). A more complete structural description is available in Rabe *et al.* (1998).

4. Structural comparison

As expected, bond distances become slightly shorter at lower temperatures, as shown in Table 2. While the Cs–Cs contacts of the individual layers do not change significantly, the distance between the ladders changes slightly [*i.e.* Cs(2F) to Cs(2K) in Fig. 3 and Cs(2) to Cs(2A) in Fig. 4, respectively]. The distance between the layers in (1B) is 5.4810 (6) Å, which increases by 1.5% to 5.564 (3) Å in (1A), reflected in a change in the density of the systems of approximately 1.2%. Figs. 3 and 4 also show that the Cs–P ladder's orientation does not change. The structures also differ slightly in the environment around the Cs atoms. The P–Cs–P bond angle measured within the 'ladder' framework (shown in Figs. 3 and 4) is 161.70 (3)° for (1B) and 165.49 (8)° for (1A). This flattening of the P–Cs–P bond angle results in a sharpening of the P–Cs–Cs bond angle measured from one 'ladder' to another. The low-temperature structure has a P–Cs–Cs bond angle of 131.30 (2)°, while the room-temperature system has a P–Cs–Cs bond angle of 128.65 (6)°.

The presence of the toluene ligand on the inversion center in (1A) resulted in the disorder of the methyl group of the η^3 -toluene ligand. Doubling the volume of the unit cell in form (1B) resulted in the ordering of the methyl group no longer being located on the inversion center. This resulted in the ordering of the methyl group with an order–disorder phase transition at 278 (2) K.

5. Conclusion

The crystal structure of $[[\text{CsPH}(\eta^6\text{-}2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2)]_2(\eta^3\text{-toluene})_{0.5}]_x$ has been shown to undergo a reversible solid-state, order–disorder phase transition at 278 (2) K. This transformation results in the doubling of a unit-cell vector, resulting in the doubling of the unit cell of the system.

Table 3
Summary of unit-cell parameters at various temperatures.

Temperature (K)	200	213	228	243	258	295
<i>a</i> (Å)	14.621 (8)	14.634 (9)	14.634 (9)	14.639 (7)	14.633 (6)	11.199 (7)
<i>b</i> (Å)	14.760 (8)	14.776 (8)	14.790 (9)	14.813 (7)	14.807 (6)	14.655 (8)
<i>c</i> (Å)	22.15 (1)	22.17 (1)	22.22 (1)	22.26 (1)	22.261 (8)	14.873 (8)
α (°)	72.10 (2)	72.07 (2)	72.00 (2)	71.89 (2)	71.89 (2)	70.47 (2)
β (°)	73.15 (1)	73.08 (1)	73.08 (1)	73.07 (2)	73.10 (2)	71.55 (3)
γ (°)	70.37 (2)	70.34 (2)	70.34 (2)	70.38 (1)	70.36 (1)	72.93 (3)
<i>V</i> (Å ³)	4190 (6)	4212 (7)	4212 (7)	4227 (5)	4223 (4)	2134 (3)
No. of reflections	233	249	214	181	191	110

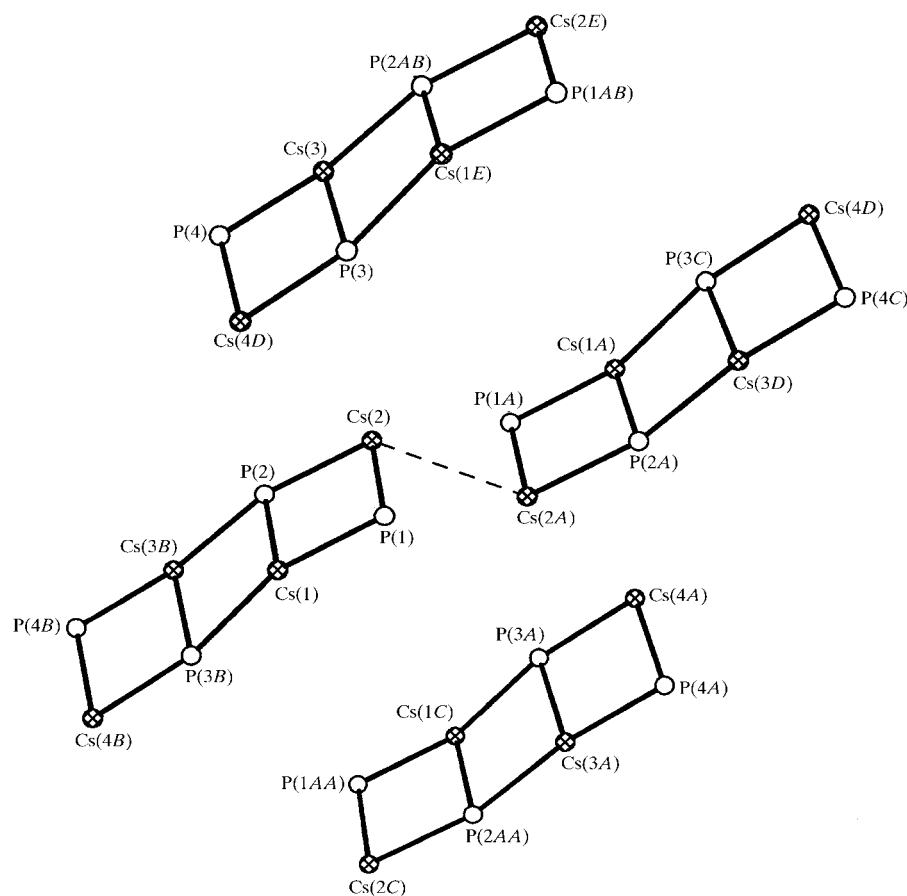


Figure 4
Ball-and-stick drawing of the Cs–P framework of (1B), as viewed down the *b* axis.

References

- Braga, D. (1992). *Chem. Rev.* **92**, 633–665.
- Braga, D., Farrugia, L. J., Gillon, A. L., Grepioni, F. & Tedesco, E. (1996). *Organometallics*, **15**, 4684–4686.
- Braga, D., Grepioni, F., Farrugia, L. J. & Johnson, B. F. G. (1994). *J. Chem. Soc. Dalton Trans.* pp. 2911–2918.
- Churchill, M. R. & Chang, S. W.-Y. (1974). *J. Chem. Soc. Chem. Commun.* pp. 248–249.
- Churchill, M. R. & Fettinger, J. C. (1990). *Organometallics*, **9**, 446–452.
- Cotton, F. A. & Troup, J. M. (1974). *J. Am. Chem. Soc.* **96**, 4155–4159.
- Dornberger-Schiff, K. (1956). *Acta Cryst.* **9**, 593–601.
- Farrugia, L. J., Senior, A. M., Braga, D., Grepioni, F., Orpen, A. G. & Crossley, J. G. (1996). *J. Chem. Soc. Dalton Trans.* pp. 631–641.
- Hsu, L.-H. & Nordman, C. E. (1983). *Science*, **220**, 604–606.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Rabe, G. W., Heize, H., Yap, G. P. A., Liablsands, L. M., Guzei, I. A. & Rheingold, A. L. (1998). *Inorg. Chem.* **37**, 4235–4245.
- Richardson, M. F., Yang, Q.-C., Novotny-Bregger, E. & Dunitz, J. D. (1990). *Acta Cryst.* **B46**, 653–660.
- Sarma, J. A. R. P. & Dunitz, J. D. (1990). *Acta Cryst.* **B46**, 784–794.
- Siemens (1994). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1994). *SHELXTL*, Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997a). *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. University of Göttingen, Germany.
- Wang, P.-W. (1979). *J. Appl. Cryst.* **12**, 239.
- Wei, C. H. & Dahl, L. F. (1969). *J. Am. Chem. Soc.* **91**, 1351–1361.