molecules of hydration for each complete chromium pyrophosphate complex. In both crystal structures, the short strong P—O—H···O—P hydrogen bonds link the complexes into hydrogen bonded dimers. The two halves of the dimer are related by a center of symmetry in the monohydrate crystal while in the dihydrate the two halves are related to each other by $2/m$ symmetry.

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Redetermination of the Space Group for [η⁵-C₅(CH₃)₅]Cl₃Ta[η²-OC(PEt₃)Si(CH₃)₃]

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Abstract. Trichloro(η^5-cyclopentadienyl)[η^2-triethyl(trimethylsilylcarbonyl)phosphonio]tantalate, $[TaCl_3(C_{10}H_{15})(C_3H_9Si)(C_6H_{15}P)]$, $M_r = 641.82$, orthorhombic, $Pca2_1$, $a = 15.820$ (4), $b = 11.314$ (4), $c = 14.809$ (5) Å, $V = 2651$ (1) Å^3, $Z = 4$, $D_x = 1.608$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 44.8$ cm^{-1}, $F(000) = 1304$, $T = 296$ K, $R = 2.85\%$ for 2428 reflections with $F_o > 3\sigma(F_o)$ and 245 parameters. The structure was originally reported [Arnold, Tilley, Rheingold, Geib & Arif (1989). *J. Am. Chem. Soc.* **111**, 149–164] in the space group *Pcam* ($R = 6.77\%$) as being fully mirror-plane disordered. A re-examination of the structure revealed that an ordered, non-centrosymmetric structure could be smoothly refined by the use of a large damping factor in the least-squares refinement, which minimized the earlier found tendency of the structure to regress toward a disordered, centrosymmetric model. Not only is the R factor much improved, but the range of bond parameters for chemically similar portions of the structure, *e.g.* the differences among the three Ta—Cl distances, has been reduced from

0.14 to 0.07 Å. However, the chemically significant structural features of the earlier report remain unchanged.

Introduction. The structure of the title complex was originally reported (Arnold, Tilley, Rheingold, Geib & Arif, 1989) as fully mirror-plane disordered in the orthorhombic space group *Pcam* ($R = 6.77\%$). We wish now to report that the non-centrosymmetric space group $Pca2_1$ ($R = 2.85\%$) is preferred by the many criteria reported below.
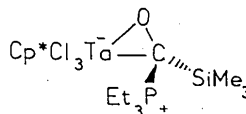
Experimental. Orange-brown crystals cleaved to a cubic shape (0.39 × 0.38 × 0.38 mm) obtained as previously reported (Arnold, Tilley, Rheingold, Geib & Arif, 1989). Nicolet $R3m/\mu$, truncated ω (Wyckoff) scans; lattice parameters from 25 reflections, $21 < 2\theta$

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

	x	y	z	U*
Ta	4342·3 (2)	2202·3 (2)	2500	37·8 (1)
P	5793 (1)	3865 (2)	1200 (2)	43 (1)
Cl(1)	3410 (1)	3937 (2)	2569 (3)	70 (1)
Cl(2)	4005 (2)	2513 (2)	876 (2)	62 (1)
Cl(3)	4683 (2)	2903 (2)	3999 (2)	63 (1)
Si	6557 (2)	2918 (2)	3057 (2)	57 (1)
O	5429 (3)	1702 (5)	2034 (4)	45 (1)
C(1)	4276 (5)	79 (8)	2776 (9)	73 (1)
C(2)	3857 (6)	592 (8)	3522 (7)	59 (1)
C(3)	3127 (5)	1173 (8)	3237 (6)	52 (1)
C(4)	3050 (5)	935 (8)	2304 (6)	58 (1)
C(5)	3764 (7)	272 (9)	2022 (8)	76 (2)
C(6)	5031 (7)	−700 (8)	2821 (11)	102 (2)
C(7)	4102 (9)	352 (12)	4494 (9)	112 (2)
C(8)	2492 (7)	1788 (9)	3834 (8)	76 (2)
C(9)	2287 (7)	1273 (11)	1735 (9)	102 (2)
C(10)	3873 (9)	−264 (12)	1090 (8)	116 (2)
C(11)	5648 (5)	2960 (6)	2203 (6)	42 (1)
C(12)	6629 (7)	4333 (10)	3725 (8)	83 (2)
C(13)	6785 (5)	4689 (8)	1261 (7)	63 (1)
C(14)	6907 (7)	5639 (9)	543 (7)	77 (2)
C(15)	5021 (6)	5012 (9)	1088 (7)	60 (1)
C(16)	5044 (8)	5898 (9)	1876 (9)	96 (2)
C(17)	5891 (7)	2966 (9)	187 (7)	68 (2)
C(18)	5559 (7)	3482 (12)	−685 (7)	92 (2)
C(19)	7601 (6)	2617 (8)	2444 (12)	88 (2)
C(20)	6503 (7)	1605 (11)	3816 (8)	91 (2)

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

$< 28°$, least-squares fit; empirical ellipsoidal absorption correction, seven reflections, $10°$ increments, $T_{max}/T_{min} = 0.133/0.100$; 2θ max. $= 55°$ ($h = +21$, $k = +15$, $l = +20$); standard reflections, 11,1,10, 1,10,11, 16,7,0, 1·5% decay (corrected); 3430 reflections collected, 3157 independent and symmetry allowed, 648 unobserved, 2509 with $F_o \geq 5\sigma(F_o)$. Solved and refined as mirror-plane disordered centrosymmetric *Pcam*; one form of molecule isolated and refined in *Pca2*$_1$ (on F for 245 parameters) with a large damping factor (see *Discussion*). All non-H atoms anisotropic, H atoms idealized [d(C—H) = 0·96 Å], isotropic contributions (rotational positions of Cp* methyl groups determined initially from found H atoms); $R(F) = 2·85$, $R(wR) = 3·44\%$, $S = 1·020$, $w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0·005$, $(\Delta/\sigma)_{max} = 0·22$, $(\Delta\rho)_{max} = 0·71$, $(\Delta\rho)_{min} = -0·61$ e Å^{-3}, atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149). An enantiomorph test was applied using a multiplicative term for f''. This refined to 0·97 (3) indicating the correctness of the hand reported. Computer programs *SHELXTL* (Sheldrick, 1985). Table 1* lists final atomic coordinates

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53180 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Ta—Cl(1)	2·457 (2)	Ta—Cl(2)	2·489 (3)
Ta—Cl(3)	2·418 (3)	Ta—O	1·936 (5)
Ta—C(1)	2·440 (9)	Ta—C(2)	2·489 (9)
Ta—C(3)	2·498 (8)	Ta—C(4)	2·514 (9)
Ta—C(5)	2·471 (10)	Ta—C(11)	2·279 (8)
P—C(11)	1·818 (9)	P—C(13)	1·828 (9)
P—C(15)	1·790 (10)	P—C(17)	1·819 (11)
Si—C(11)	1·916 (9)	Si—C(12)	1·884 (12)
Si—C(19)	1·915 (12)	Si—C(20)	1·866 (13)
O—C(11)	1·486 (9)	C(1)—C(2)	1·413 (15)
C(1)—C(5)	1·397 (17)	C(1)—C(6)	1·486 (13)
C(2)—C(3)	1·394 (13)	C(2)—C(7)	1·515 (16)
C(3)—C(4)	1·414 (12)	C(3)—C(8)	1·509 (14)
C(4)—C(5)	1·419 (14)	C(4)—C(9)	1·521 (14)
C(5)—C(10)	1·517 (17)	C(13)—C(14)	1·524 (15)
C(15)—C(16)	1·538 (16)	C(17)—C(18)	1·512 (16)
Ta—CNT*	2·175 (8)		
CNT—Ta—Cl(1)	109·7 (2)	P—C(11)—Si	117·3 (4)
CNT—Ta—Cl(2)	100·5 (2)	P—C(11)—O	115·5 (6)
CNT—Ta—Cl(3)	102·7 (2)	P—C(13)—C(14)	115·8 (7)
CNT—Ta—C(11)	145·8 (3)	P—C(17)—C(18)	117·3 (8)
CNT—Ta—O	107·1 (3)	Cl(1)—Ta—Cl(3)	80·4 (1)
Cl(1)—Ta—Cl(2)	78·4 (1)	Cl(1)—Ta—O	141·3 (2)
Cl(2)—Ta—Cl(3)	152·7 (1)	Cl(3)—Ta—O	103·0 (2)
Cl(2)—Ta—O	83·5 (2)	Cl(2)—Ta—C(1)	107·0 (3)
Cl(1)—Ta—C(11)	104·6 (2)	Cl(2)—Ta—C(11)	87·4 (2)
Cl(3)—Ta—C(11)	81·5 (2)	O—Ta—C(11)	40·3 (2)
C(11)—P—C(13)	113·5 (4)	C(11)—P—C(13)	110·8 (4)
C(11)—P—C(17)	111·7 (4)	C(13)—P—C(15)	102·7 (4)
C(15)—P—C(17)	112·8 (5)	C(13)—P—C(17)	104·7 (5)
C(11)—Si—C(19)	109·8 (6)	C(11)—Si—C(12)	111·8 (4)
C(11)—Si—C(20)	112·5 (5)	C(12)—Si—C(19)	110·4 (5)
C(19)—Si—C(20)	100·6 (5)	C(12)—Si—C(20)	111·3 (6)
C(2)—C(1)—C(5)	106·8 (8)	Ta—O—C(11)	82·4 (4)
C(2)—C(1)—C(6)	125·9 (11)	C(5)—C(1)—C(6)	126·5 (11)
C(1)—C(2)—C(3)	110·2 (9)	C(3)—C(2)—C(7)	125·7 (9)
C(1)—C(2)—C(7)	123·3 (9)	C(4)—C(3)—C(8)	127·1 (8)
C(2)—C(3)—C(4)	106·2 (8)	C(5)—C(4)—C(9)	127·0 (9)
C(2)—C(3)—C(8)	126·3 (9)	C(4)—C(5)—C(10)	124·7 (10)
C(3)—C(4)—C(5)	108·6 (8)	Ta—C(11)—Si	123·0 (4)
C(3)—C(4)—C(9)	124·3 (8)	Ta—C(11)—O	57·4 (3)
C(1)—C(5)—C(4)	108·0 (9)	Si—C(11)—O	105·3 (5)
C(1)—C(5)—C(10)	126·8 (10)	P—C(15)—C(16)	112·7 (7)
Ta—C(11)—P	118·9 (4)		

*CNT = centroid C(1) to C(5).

and Table 2 bond lengths and angles. Fig. 1 shows the molecular structure of the complex and Fig. 2 shows a unit-cell packing stereoview.

Discussion. Crystallographers routinely face the problem of determining the presence or absence of an inversion center for space groups not uniquely determined from systematic absences. The pairs $P2_1{:}P2_1/m$, $Cc{:}C2/c$, $Pna2_1{:}Pnam$ and $Pca2_1{:}Pcam$ are the ones most frequently encountered* and those with mirror-plane ambiguities often prove the most troublesome. Recourse to secondary methods such as an examination of non-linear optical properties or piezoelectric effects often fails to resolve matters due to the uncertain contributions of impurities; also, these methods require equipment not found in most

* The pair $P1{:}P\bar{1}$ is not included due to the very low probability of encountering $P1$. Of 347 triclinic structures we have done, the only non-centrosymmetric ones encountered were structures of resolved chiral molecules.

laboratories. The statistical distribution of E values is also often not helpful, especially in situations where heavy atoms reside on special positions. Crystallographers are most often left without 'hard' evidence for inversion centers and ultimately must rely on the chemical credibility of the results of refinement.

In the present case, E statistics appeared unambiguously centrosymmetric [$|E^2 - 1| = 0.98$, (theor. $= 0.97$)], initial refinement of the Ta, Cl, P and Si atoms in both $Pcam$ and $Pca2_1$ produced essentially identical difference maps displaying the 'obvious' presence of mirror-plane symmetry. Therefore, the refinement of the originally reported characterization (Arnold, Tilley, Rheingold, Geib & Arif, 1989) was continued as a disordered, centrosymmetric structure and the final results were at least a chemically reasonable and adequate verification of a compound already well established by spectroscopic methods.

More recently, experiences with another structure in the same pair of space groups led us to explore the effects of incorporating large damping factors in least-squares refinement as a way of restraining the inexorable tendency of nearly-centrosymmetric, non-centrosymmetric structures to progress toward a centrosymmetric conclusion. The successful application of this procedure required refinement of a model

Fig. 1. Molecular structure and labeling scheme for the title complex drawn with 45% thermal ellipsoids.

Fig. 2. Unit-cell stereoview down the b axis (c horizontal).

containing a complete, or very nearly complete, set of non-H atoms, and consistently failed when a less complete model was considered. Since an incomplete model is all that is available in the early stages of structure solution and refinement, all such refinements, even with damping, showed persuasive (and misleading) signs of centrosymmetry. Therefore, our strategy for such structures has been to pursue the centrosymmetric model until all non-H atoms have been located, often requiring tedious examinations of chemically ridiculous models for new atoms from subsequent difference maps. When a more-or-less complete image of a single, 'ordered' structure is apparent in the confusion of doubled images, all atoms extraneous to this model are deleted, the inversion center removed, and refinement attempted with a large damping factor to restrict large excursions in positional parameters. [Our efforts have been confined to the *SHELXTL* program (Sheldrick, 1985) which uses the Marquardt (1963) method; in these routines we have used a factor of 250–500.] The result, as in the present case, is often spectacular.

In the original disclosure of the title structure, the discussion of structural features was prudently minimized. However, none of the earlier reported bond parameters, when compared to those which we now report, is sufficiently different to cause an important change in the chemical interpretation of the structure. Perhaps the most chemically significant change has been in the C(11)—O distance: originally 1.43 (3), now 1.486 (9) Å, although this difference is almost within the reported e.s.d.'s. The new, longer value reflects an expected greater metal-to-ligand donation into a ligand C—O π^* level; this value is the longest C—O distance seen for any of the analogous compounds reported in the original paper, an observation in keeping with the presence of PEt$_3$, a significantly better sigma donor than was present in any of the analogues. Also, chemically similar parameters are now found in considerably narrower ranges, although the averages have not changed. For example, as originally reported, the range of Ta—Cl distances was 2.389 (7) to 2.531 (7) (av. 2.454 Å), and is now 2.418 (3) to 2.489 (3) (av. 2.455 Å).

Jones (1984), Marsh (1986), Baur & Tillmanns (1986) and Harlow (1987) have in recent years presented warnings to crystallographers about failures to include all symmetry elements in space group determinations. 'In cases where diffraction data do not provide a clear choice between a centrosymmetric and a non-centrosymmetric space group, it is better to opt for the centrosymmetric description even though disorder may result' (Marsh, 1986). These warnings, accompanied by an approximate occurrence of inversion centers in 80–85% of routine structures, may have overly encouraged searches for
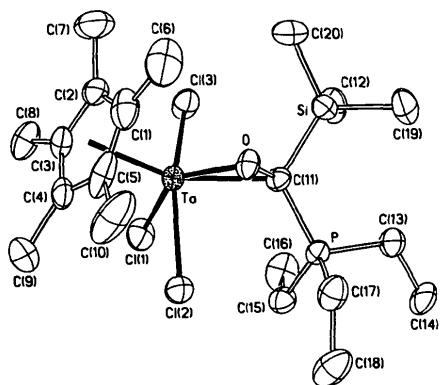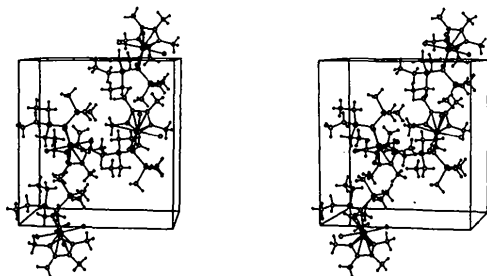
centrosymmetry where none existed, and dissuaded elimination of symmetry when preliminary results indicated its presence.

From among over 1300 data collections processed by our laboratory in the past eight years, about 60 have been consigned to our 'morgue' for unsolved structures: those that defied our every attempt to extract a chemically sensible product. An examination of the space groups of these moribund structures revealed that more than 3/4 were in ambiguous space groups, with greater than half occurring in the systems mentioned above. In the past several months, we have found that the application of the procedures outlined above allowed us to solve suc-

cessfully about 20 of these structures. Not one of these re-examinations revealed that the *absence* of symmetry was the cause of the original difficulty.

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The Structure of a Platinum Polyfluorophenylthiolate, trans-[Pt(SC₆F₅)₂(SEt₂)₂]

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Abstract. *trans*-Bis(diethyl sulfide)bis(pentafluorobenzenethiolato)platinum(II), [Pt(C₆F₅S)₂(C₄H₁₀S)₂], $M_r = 773.71$, monoclinic, $P2_1/n$, $a = 10.775\,(3)$, $b = 12.842\,(7)$, $c = 10.052\,(3)$ Å, $\beta = 113.65\,(2)°$, $V = 1274$ Å³, $Z = 2$, $D_c = 1.99$, $D_x = 2.02$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 59.58$ cm⁻¹, $F(000) = 743.86$, room temperature, final $R = 0.0315$ for 2212 unique observed reflexions. The Pt atom lies on an inversion centre, and shows *trans* square planar geometry. Not only are the SC₆F₅ groups planar but so are the non-H atoms of the S(C₂H₅)₂ moieties. The SC₆F₅ moieties have bond distances Pt—S 2.323 (1) and S—C 1.760 (7) Å; the S(C₂H₅)₂ has Pt—S 2.302 (1) and S—C 1.805 (6) and 1.808 (5) Å.

Introduction. There is some considerable interest in homodonor (sulfur) compounds of the platinum metals in view of their relevance to biological systems and catalytic processes and their usefulness in chemical synthesis (Hagen, Stephan & Holm, 1982; Roesky, 1986; Ueyama, Sugawara, Sasaki, Nakamura, Yamashita, Wakatsuk, Yamazaki & Yasuoka, 1988). In a number of cases unusual structures are stabilized (Catala, Cruz-Garritz, Hills,

Hughes, Richards, Terreros & Torrens, 1987; Catala, Cruz-Garritz, Hills, Hughes, Richards, Sosa & Torrens, 1987).

Experimental. The title compound was formed in 81% yield from the reaction of Pb(SC₆F₅)₂ with [PtCl₂(SEt₂)₂] in acetone solution and subsequent addition of water (after filtering off of PbCl₂). The yellow crystals were recrystallized from acetone. X-ray reflexion data from a small (approx. 0.15 × 0.20 × 0.25 mm) block-shaped crystal were collected on a Nicolet *R3M* 4-circle automatic diffractometer operating in the ω-scan mode and using Mo *Kα* radiation (graphite monochromator). The unit-cell parameters were determined by least squares from the setting angles of 25 well centred reflexions in the range $5 < 2\theta < 23°$. Density by flotation in a mixture of iodobenzene and toluene. An empirical absorption correction was applied from azimuthal scans on seven reflexions (252 measurements) and gave maximum and minimum transmission factors of 0.379 and 0.287 respectively. Reflexion data in the range $6.5 < 2\theta < 55°$ and having $0 < h < 14$, $0 < k < 17$, and $-14 < l < 14$ were collected. Two check reflexions were monitored every 100 reflexions and showed