Absorption correction:
  ψ scan (North *et al.*, 1968)
  $T_{\min} = 0.703$, $T_{\max} = 0.825$
2000 measured reflections
1917 independent reflections
1563 reflections with
  $I > 2\sigma(I)$

$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -13 \rightarrow 13$
3 standard reflections
  every 100 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.079$
$S = 1.063$
1917 reflections
161 parameters
All H-atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 3.0416P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.262$ e Å^{-3}
$\Delta\rho_{\min} = -0.347$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0	1/2	0	0.02384 (13)
O1	0	0.5453 (2)	1/4	0.0319 (6)
O2	−0.07246 (13)	0.37887 (12)	0.04052 (16)	0.0270 (4)
O3	−0.14417 (16)	0.32996 (15)	−0.16071 (18)	0.0409 (5)
N1	0.13576 (15)	0.42477 (15)	0.05563 (19)	0.0253 (4)
N3	0.24643 (18)	0.31795 (17)	0.1727 (2)	0.0333 (5)
C2	0.1504 (2)	0.3601 (2)	0.1528 (3)	0.0313 (6)
C4	0.2998 (2)	0.35642 (19)	0.0806 (2)	0.0300 (5)
C5	0.4003 (2)	0.3389 (2)	0.0558 (3)	0.0433 (7)
C6	0.4280 (3)	0.3899 (3)	−0.0470 (4)	0.0542 (9)
C7	0.3590 (3)	0.4566 (3)	−0.1233 (4)	0.0521 (8)
C8	0.2601 (2)	0.4741 (2)	−0.0975 (3)	0.0387 (7)
C9	0.23025 (19)	0.42381 (18)	0.0061 (2)	0.0272 (5)
C10	−0.13374 (17)	0.32638 (17)	−0.0402 (2)	0.0235 (5)
C11	−0.20004 (19)	0.25624 (18)	0.0222 (2)	0.0262 (5)

Table 5. *Selected geometric parameters (Å, °) for (II)*

Cu—O1	2.6683 (7)	N1—C2	1.315 (3)
Cu—O2	1.9461 (15)	N1—C9	1.407 (3)
Cu—N1	2.016 (2)	N3—C2	1.346 (3)
O2—C10	1.260 (3)	N3—C4	1.373 (3)
O3—C10	1.238 (3)		
O1—Cu—O2	83.88 (7)	C2—N3—C4	107.6 (2)
O1—Cu—N1	88.92 (7)	N1—C2—N3	113.3 (2)
O2—Cu—N1	87.49 (7)	N3—C4—C5	131.9 (3)
Cu—O1—Cu$^{\rm i}$	153.93 (12)	N3—C4—C9	105.7 (2)
C10—O2—Cu	125.81 (15)	N1—C9—C4	108.6 (2)
C2—N1—C9	104.9 (2)	O2—C10—O3	126.7 (2)
C2—N1—Cu	123.08 (18)	O2—C10—C11	113.6 (2)
C9—N1—Cu	131.97 (16)	O3—C10—C11	119.7 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O3$^{\rm i}$	0.81 (3)	1.98 (4)	2.775 (2)	167 (4)
N3—H3$\cdots$O3$^{\rm ii}$	0.83 (3)	2.02 (3)	2.831 (3)	167 (3)

Symmetry codes: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The title structures were solved by the conventional Patterson method and refined by full-matrix least-squares calculations. All non-H atoms were refined anisotropically. All H atoms were located from a difference synthesis and refined isotropically.

For both compounds, data collection: *P*3 software; cell refinement: *P*3 software; data reduction: *XDISK* in *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *XP* in *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*97.

This work was partly supported by the Polish Scientific Research Committee (KBN) (grant 560/T09/97/12).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1272). Services for accessing these data are described at the back of the journal.

References

Kálmán, A. & Párkányi, L. (1997). *Adv. Mol. Struct. Res.* **3**, 189–226.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *SHELXTL*/*PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997*a*). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Tosik, A. & Bukowska-Strzyżewska, M. (1992). *J. Crystallogr. Spectrosc. Res.* **22**, 225–229.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*a*). *Acta Cryst.* C**51**, 1985–1987.
Tosik, A., Sieroń, L. & Bukowska-Strzyżewska, M. (1995*b*). *Acta Cryst.* C**51**, 1987–1989.
Verdaguer, M., Gouteron, J., Jeannin, S., Jeannin, Y. & Kahn, O. (1984). *Inorg. Chem.* **23**, 4291–4296.

Acta Cryst. (1998). C**54**, 1435–1438

A Dinuclear Vanadyl–Oxalate Compound

Li-Min Zheng,[a] Helmut W. Schmalle,[b] Sylvie Ferlay[c] and Silvio Decurtins[c]

[a]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China,* [b]*Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and* [c]*Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland. E-mail: schmalle@aci.unizh.ch*

(Received 13 February 1998; accepted 5 May 1998)

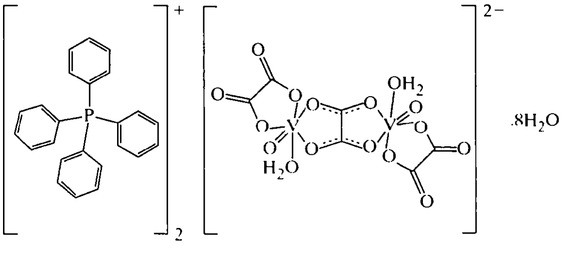
Abstract

The title compound, bis(tetraphenylphosphonium) μ-oxalato-$O^1,O^2:O^{1'},O^{2'}$-bis[aqua(oxalato-O^1,O^2)oxovanadium(IV)] octahydrate, $[(C_6H_5)_4P]_2[V_2O_2(C_2O_4)_3(H_2O)_2].8H_2O$, consists of an anionic vanadyl dimer linked by an oxalate ligand and additionally coordinated by two non-bridging oxalate and two water mol-

ecules. Both the bridging and non-bridging oxalates act as bidentate chelating ligands, forming five-membered rings with the metal centres. The V^{IV} atoms are six-coordinated, forming a distorted octahedral geometry. A two-dimensional O—H···O hydrogen-bonding network of water molecules and oxalate O atoms stabilizes the structure.

Comment

In order to extend our knowledge of the structural, magnetic and photophysical properties of inorganic bimetallic polymers of the type M^{II}-M^{III}, based on oxalato-bridged networks (Decurtins *et al.*, 1994, 1996; Pellaux *et al.*, 1997), we are currently studying the corresponding vanadium compounds. While using $[V^{III}(ox)_3]^{3-}$ (ox is oxalate) as a 'building block', we allowed it to react with nickel(II), expecting a heterometallic compound containing V^{III} and Ni^{II}. However, we obtained the title compound, (I), where V^{III} has been oxidized to V^{IV} by water and oxygen, while forming the oxovanadium(IV) centres. To the best of our knowledge, no crystal structure consisting of oxovanadium(IV) ions and oxalate bridging ligands has been reported so far. The crystal structure of (I) consists of dimeric oxovanadium(IV) anions with one bridging oxalate (*A*) and two non-bridging oxalates (*B*), as well as tetraphenylphosphonium cations and eight water molecules of crystallization. The five-membered V—O—C—C—O rings are in envelope conformations.



(I)

A displacement ellipsoid plot of the title complex with the atom-labelling scheme is shown in Fig. 1. Two V atoms are bridged through an oxalate anion. An inversion centre is located between the C atoms of this oxalate and generates the dimeric unit. The environment of each V atom consists of six O atoms.

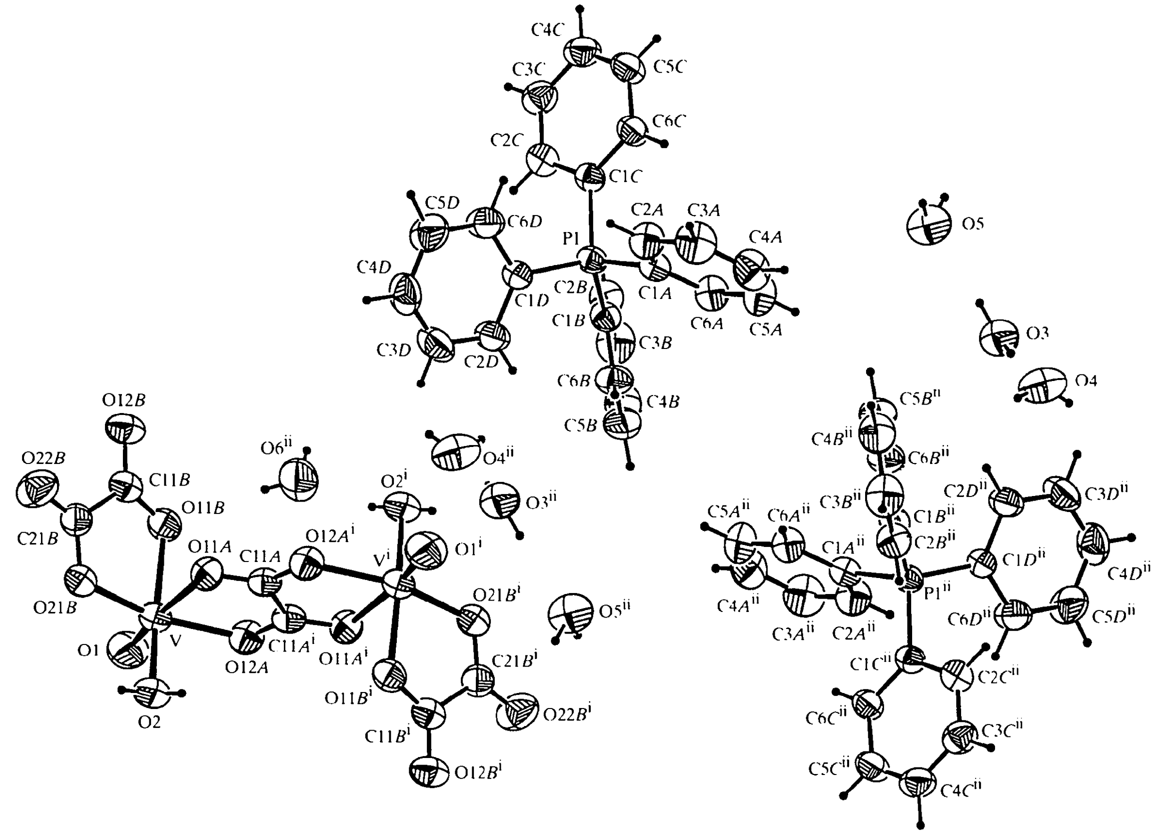


Fig. 1. Displacement ellipsoid plot of the complete structure of (I), drawn with *PLATON* (Spek, 1990). Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii. [Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, 1 - y, 1 - z$.]

The octahedral distortions can be described by the deviation of the V atom from the three equatorial least-squares planes. These deviations are 0.003 (1) Å for the plane defined by O1, O2, O11*A* and O11*B*, 0.016 (1) Å for the O1, O12*A*, O11*A* and O21*B* plane, and 0.361 (1) Å for the O2, O12*A*, O11*B* and O21*B* plane. This last deviation is related to the short V—O1 distance of 1.585 (2) Å, which is in agreement with the V═O double bond of an oxovanadium(IV) entity. The other position is occupied by the oxalate O11*A* atom, with an elongated V—O11*A* distance [2.275 (2) Å]. In contrast to the (acac)$V^{IV}O(ox)V^{IV}O$(acac) compound (acac is acetylacetonate; Julve *et al.*, 1984), where the two O atoms from oxovanadium(IV) and the water molecule are in *trans* positions, in (I), they are in *cis* positions. The V—O bond lengths in (I) corresponding to the non-bridging oxalate ligands *B* are similar to those of the mononuclear vanadyl compound $(NH_4)_2[V^{IV}O(C_2O_4)_2(H_2O)].H_2O$ (Oughtred *et al.*, 1976). The oxalate group *A* is planar, with the largest deviations of −0.002 (1) Å for C11*A* and 0.002 (1) Å for C11A^{i} [symmetry code: (i) $-x$, $-y$, $-z$]. The V atoms reside in this plane, with a deviation of 0.022 (3) Å. The largest deviations in the oxalate group *B* plane are −0.015 (1) Å for O11*B* and 0.015 (1) Å for O21*B*. The V atoms are pulled out of this plane by 0.210 (2) Å. The planarity of the oxalato groups is also shown by the O—C—C—O torsion angles given in Table 1.

The $[PPh_4]^+$ cation exhibits normal bond lengths and angles. The crystal packing of the oxovanadium(IV) dimers in the unit cell exhibits a two-dimensional layered structure through extensive hydrogen bonding with lattice water (Figs. 2 and 3). The $[PPh_4]^+$ cations are intercalated between these layers. There are weak C—H···O interactions, with H···O distances in the range 2.60–2.71 Å, between the $[PPh_4]^+$ cations and the O atoms of the non-bridging oxalato groups and water. However, there is only one C—H···O hydrogen bond involving the oxovanadium(IV) group (Table 2).

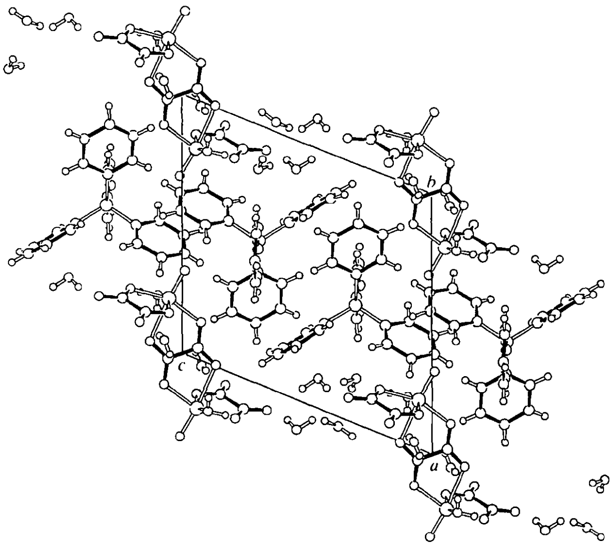


Fig. 2. Packing diagram (*SCHAKAL86*; Keller, 1986) viewed along the a^* axis. Note the solvent water around centres of symmetry.

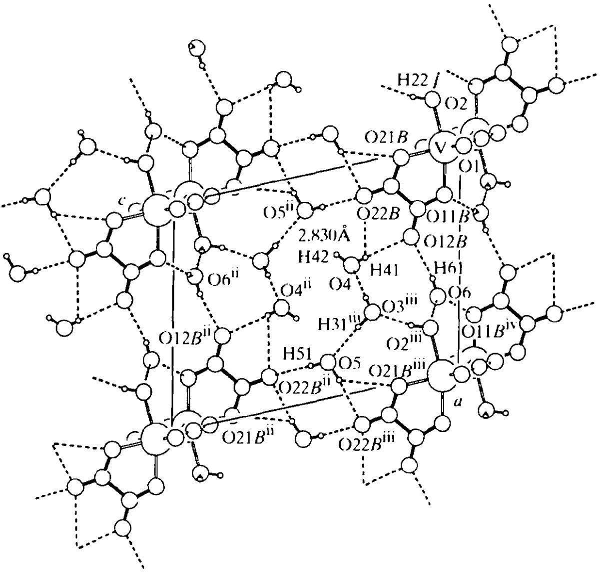


Fig. 3. *PLUTON* (Spek, 1990) plot showing the hydrogen-bonding scheme between the water molecules and the oxalato groups of (I) in the **ac** projection. $[PPh_4]^+$ cations have been omitted for clarity. The non-bonding distance of 2.830 Å between atoms H42 and $O5^{ii}$ is indicated. Other geometrical details are given in Table 2, together with the symmetry codes used.

Experimental

To an aqueous solution (20 ml) of $K_3[V^{III}(ox)_3].3H_2O$ (0.243 g, 0.5 mmol) and $(PPh_4)Cl$ (0.187 g, 0.5 mmol) was added $Ni^{II}(NO_3)_2.6H_2O$ (0.145 g, 0.5 mmol) in H_2O (5 ml). The light-green precipitate was filtered off. The title compound, (I), was crystallized as green platelets by evaporation of the filtrate. Analysis, calculated for $C_{27}H_{30}O_{12}PV$: C 54.07, H 4.35%; found: C 51.56, H 4.77%.

Crystal data

$(C_{24}H_{20}P)_2[V_2O_2(C_2O_4)_3(H_2O)_2].8H_2O$
$M_r = 1256.88$
Triclinic
$P\overline{1}$
$a = 9.571$ (4) Å
$b = 12.773$ (6) Å
$c = 13.486$ (6) Å
$\alpha = 66.39$ (3)°
$\beta = 74.97$ (3)°
$\gamma = 80.84$ (3)°
$V = 1456.1$ (11) Å^3
$Z = 1$
$D_x = 1.433$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.7$–11.4°
$\mu = 0.457$ mm^{-1}
$T = 296$ (2) K
Prism
0.66 × 0.40 × 0.35 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.831$, $T_{\max} = 0.869$
8795 measured reflections
8461 independent reflections
5482 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\max} = 29.96°$
$h = -12 \rightarrow 13$
$k = -16 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections every 400 reflections frequency: 180 min intensity decay: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.121$
$S = 1.092$
8461 reflections
485 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.7029P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.275$ e Å^{-3}
$\Delta\rho_{\min} = -0.429$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0068 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

V—O1	1.5854 (17)	V—O12*A*	2.0233 (17)
V—O21*B*	1.9831 (18)	V—O2	2.0443 (18)
V—O11*B*	2.0159 (16)	V—O11*A*	2.2745 (18)
O1—V—O21*B*	103.71 (9)	O11*B*—V—O2	158.26 (6)
O1—V—O11*B*	101.73 (9)	O12*A*—V—O2	89.30 (8)
O21*B*—V—O11*B*	81.14 (7)	O1—V—O11*A*	172.79 (8)
O1—V—O12*A*	96.64 (9)	O21*B*—V—O11*A*	83.49 (6)
O21*B*—V—O12*A*	159.55 (6)	O11*B*—V—O11*A*	79.05 (6)
O11*B*—V—O12*A*	93.02 (7)	O12*A*—V—O11*A*	76.15 (6)
O1—V—O2	99.46 (9)	O2—V—O11*A*	80.55 (7)
O21*B*—V—O2	89.20 (7)		

O12*B*—C11*B*—C21*B*—O22*B*	−1.2 (3)
O11*B*—C11*B*—C21*B*—O22*B*	178.50 (19)
O12*B*—C11*B*—C21*B*—O21*B*	178.64 (18)
O11*B*—C11*B*—C21*B*—O21*B*	−1.6 (2)
O11*A*—C11*A*—C11*A*$^{\rm i}$—O11*A*$^{\rm i}$	180.0
O11*A*—C11*A*—C11*A*$^{\rm i}$—O12*A*	180.0

Symmetry code: (i) $-x, -y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H21···O6$^{\rm i}$	0.80 (4)	1.98 (4)	2.760 (3)	164 (4)
O2—H22···O3	0.84 (2)	1.83 (3)	2.656 (3)	168 (3)
O3—H31···O5$^{\rm i}$	0.87 (3)	1.96 (3)	2.817 (3)	172 (3)
O3—H32···O4$^{\rm i}$	0.81 (3)	1.93 (3)	2.732 (3)	176 (3)
O4—H41···O12*B*	0.71	2.23	2.937 (3)	176
O4—H41···O22*B*	0.71	2.56	2.909 (3)	113
O5—H51···O22*B*$^{\rm ii}$	0.85 (4)	2.10 (4)	2.952 (3)	175 (4)
O5—H52···O21*B*$^{\rm iii}$	0.87 (4)	2.55 (4)	3.171 (3)	129 (3)
O5—H52···O22*B*$^{\rm iii}$	0.87 (4)	2.12 (4)	2.985 (3)	175 (4)
O6—H61···O12*B*	0.76 (3)	2.03 (3)	2.782 (3)	169 (3)
O6—H62···O11*B*$^{\rm iv}$	0.76 (4)	2.28 (4)	3.003 (3)	160 (4)
C6*D*—H6*D*···O1$^{\rm v}$	0.95 (3)	2.27 (3)	3.145 (3)	153 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $1-x, -y, 1-z$; (iii) $1+x, y, z$; (iv) $1-x, -y, -z$; (v) $1+x, y, 1+z$.

The positions of all 30 H atoms were determined from difference electron-density maps. They were refined with isotropic displacement parameters, except for the H atoms bonded to O4, whose positional parameters were fixed and only the displacement parameters refined, since in preliminary refinement cycles one of the H atoms lacked hydrogen bonding. The $U_{\rm iso}$ of H42 is 0.22 (2) Å^2, the highest value observed of all the H atoms. This may be due to the fact that this H atom has no acceptor atom for intermolecular interactions. However, further inspection of the O4—H42 environment with *PLATON* (Spek, 1990) showed an intermolecular H42···C3*B* distance of 3.04 (14) Å, where C3*B* belongs to phenyl ring *B* of the tetraphenylphosphonium cation. This distance is much greater than the value of 2.80 Å observed for H···C$_{\rm arene}$, as reported by Ferguson *et al.* (1994, and references therein). The **ac** projection (Fig. 3) shows the two-dimensional layer of the hydrogen-bonding scheme. The non-bonding H42···O5$^{\rm ii}$ distance is 2.830 Å, which exceeds the sum of the van der Waals radii (2.72 Å) by 0.11 Å, but the O4—H42···O5$^{\rm ii}$ angle of 124° indicates an approximation of a non-bonding interaction that fits into the hydrogen-bonding network [symmetry code: (ii) $1-x, -y, 1-z$]. The problem of doubtful and wrong positions of H atoms in X-ray structure analyses is extensively discussed by Huber-Buser (1971).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990) and *SCHAKAL*86 (Keller, 1986). Software used to prepare material for publication: *SHELXL*97.

We express gratitude to the Swiss National Science Foundation for financial support under project No. 20-45750.95.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1188). Services for accessing these data are described at the back of the journal.

References

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
Decurtins, S., Schmalle, H. W., Oswald, H. R., Linden, A., Ensling, J., Gütlich, P. & Hauser, A. (1994). *Inorg. Chim. Acta*, **216**, 65–73.
Decurtins, S., Schmalle, H. W., Pellaux, R., Schneuwly, P. & Hauser, A. (1996). *Inorg. Chem.* **35**, 1451–1460.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Ferguson, G., Gallagher, J. F., Glidewell, C. & Zakaria, C. M. (1994). *Acta Cryst.* C**50**, 70–73.
Huber-Buser, E. (1971). *Z. Kristallogr.* **133**, 150–167.
Julve, M., Verdaguer, M., Charlot, M.-F., Kahn, O. & Claude, R. (1984). *Inorg. Chim. Acta*, **82**, 5–12.
Keller, E. (1986). *SCHAKAL*86. *A Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.
Oughtred, R. E., Raper, E. S. & Shearer, H. M. M. (1976). *Acta Cryst.* B**32**, 82–87.
Pellaux, R., Schmalle, H. W., Huber, R., Fischer, P., Hauss, T., Ouladdiaf, B. & Decurtins, S. (1997). *Inorg. Chem.* **36**, 2301–2308.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.