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Tetraphenylphosphonium Trichloro-(2,5-dimethylhex-3-yne-2,5-diol)platinate(II)

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Abstract. $[P(C_6H_5)_4]^+[PtCl_3(C_8H_{14}O_2)]^-$, monoclinic, $P2_1/c$, $a=9.336$ (2), $b=27.402$ (2), $c=13.713$ (4) Å, $\beta=112.87$ (2)°, $D_m=1.61$ (1), $Z=4$, $D_c=1.608$ g cm⁻³. The complex was prepared as the potassium salt in solution, by method (1) of Chatt, Guy, Duncanson & Thompson [*J. Chem. Soc.* (1963), pp. 5170–5183]. Several attempts to obtain crystals suitable for single-crystal X-ray analysis were unsuccessful. A light-yellow powder was precipitated by adding the stoichiometric amount of tetraphenylphosphonium chloride. Trans-

parent yellow crystals of the tetraphenylphosphonium salt of the complex were grown from dichloromethane-benzene solutions, m.p. 185–186°C.

Introduction. The cell constants and their estimated standard deviations were determined from a least-squares fit of 55 2θ values measured on $h0l$ and $0kl$ Weissenberg photographs, calibrated with superimposed ZnO powder lines and taken with Cu $K\alpha$ radiation at $\sim 23^\circ\text{C}$. Systematic absences were observed for

Table 1. Final positional ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$)Estimated standard deviations are given in parentheses. Coefficients b_{ij} are defined by the expression

$$T = \exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₂	<i>b</i> ₂₃	<i>b</i> ₃₃
Pt	1276 (1)	822 (0)	2148 (1)	195 (1)	- 9 (1)	90 (1)	12 (0)	-10 (1)	81 (1)
Cl(1)	589 (8)	720 (2)	354 (4)	395 (14)	-54 (6)	167 (12)	25 (1)	-26 (4)	96 (4)
Cl(2)	1573 (6)	1646 (2)	1960 (4)	259 (10)	-14 (4)	99 (10)	15 (1)	1 (3)	107 (4)
Cl(3)	1914 (8)	925 (2)	3931 (4)	387 (14)	-14 (6)	117 (12)	25 (1)	-16 (4)	88 (4)
C(1)	3049 (47)	- 652 (14)	2383 (63)	479 (97)	194 (50)	590 (214)	34 (11)	-28 (63)	994 (171)
C(2)	3326 (37)	- 179 (12)	2511 (36)	404 (72)	210 (39)	291 (114)	30 (7)	34 (34)	450 (68)
C(3)	1862 (37)	24 (8)	2380 (20)	745 (92)	-41 (27)	277 (75)	3 (4)	-13 (14)	128 (24)
C(4)	413 (30)	117 (11)	2304 (20)	367 (57)	-70 (32)	257 (59)	43 (8)	- 3 (20)	129 (23)
C(5)	-1280 (39)	- 8 (13)	2152 (28)	496 (79)	-123 (41)	499 (99)	46 (9)	-25 (29)	247 (40)
C(6)	-1305 (39)	- 552 (12)	2038 (27)	587 (87)	-175 (40)	413 (99)	32 (7)	8 (26)	250 (40)
C(7)	3927 (42)	20 (18)	1761 (39)	449 (87)	114 (55)	723 (142)	75 (14)	79 (50)	436 (73)
C(8)	4452 (45)	-73 (23)	3617 (37)	406 (82)	296 (71)	-182 (101)	121 (22)	-80 (56)	261 (53)
C(9)	-1235 (42)	96 (18)	3269 (30)	467 (86)	-17 (57)	431 (104)	81 (15)	- 6 (40)	218 (42)
C(10)	-2412 (31)	230 (13)	1212 (40)	233 (51)	25 (31)	185 (98)	39 (9)	199 (43)	521 (78)
P	6324 (4)	2719 (2)	1351 (3)	124 (6)	4 (3)	55 (7)	16 (1)	- 7 (2)	64 (3)
C(11)	5807 (17)	2126 (7)	748 (12)	122 (24)	10 (14)	9 (26)	19 (4)	- 2 (10)	55 (11)
C(12)	4579 (18)	1859 (7)	790 (13)	147 (27)	-10 (14)	26 (28)	17 (4)	- 1 (10)	65 (13)
C(13)	4279 (19)	1384 (8)	373 (15)	152 (29)	- 9 (16)	27 (34)	18 (4)	- 5 (13)	107 (17)
C(14)	5227 (21)	1183 (8)	-84 (17)	179 (32)	-16 (17)	102 (39)	18 (4)	- 9 (14)	132 (20)
C(15)	6463 (24)	1456 (9)	-124 (17)	227 (39)	32 (23)	117 (44)	34 (6)	-34 (16)	112 (20)
C(16)	6786 (21)	1917 (7)	313 (15)	200 (33)	-25 (17)	132 (38)	18 (4)	-32 (13)	105 (17)
C(17)	6665 (17)	3118 (6)	438 (12)	134 (24)	-14 (13)	81 (28)	15 (4)	- 5 (10)	73 (13)
C(18)	8123 (21)	3317 (8)	669 (17)	193 (33)	-14 (18)	141 (41)	21 (5)	13 (14)	120 (19)
C(19)	8304 (26)	3635 (12)	-75 (21)	237 (44)	-88 (29)	187 (54)	48 (8)	20 (23)	160 (26)
C(20)	7080 (28)	3733 (12)	-1042 (19)	285 (49)	34 (31)	121 (49)	52 (9)	37 (21)	99 (20)
C(21)	5655 (22)	3525 (8)	-1257 (16)	215 (36)	- 7 (18)	104 (39)	19 (4)	- 4 (13)	100 (18)
C(22)	5457 (21)	3223 (8)	- 517 (14)	223 (34)	- 5 (17)	83 (34)	18 (4)	- 5 (11)	75 (14)
C(23)	4801 (17)	2960 (6)	1718 (12)	151 (25)	1 (13)	56 (27)	10 (3)	- 6 (9)	63 (12)
C(24)	4490 (21)	2715 (8)	2488 (14)	216 (34)	10 (18)	117 (36)	24 (5)	- 3 (12)	74 (14)
C(25)	3313 (20)	2878 (7)	2812 (15)	190 (33)	- 1 (15)	126 (38)	17 (4)	- 7 (12)	101 (16)
C(26)	2492 (18)	3301 (8)	2344 (14)	127 (27)	15 (17)	10 (30)	30 (5)	- 8 (13)	73 (14)
C(27)	2861 (21)	3564 (8)	1599 (16)	205 (34)	50 (17)	89 (38)	18 (4)	2 (13)	106 (18)
C(28)	4030 (18)	3387 (7)	1254 (14)	142 (27)	14 (15)	63 (31)	19 (4)	0 (11)	87 (15)
C(29)	8002 (15)	2666 (5)	2541 (12)	92 (20)	- 5 (11)	18 (25)	10 (3)	0 (9)	78 (12)
C(30)	8810 (21)	2225 (8)	2806 (17)	178 (30)	22 (18)	26 (35)	21 (4)	- 7 (14)	110 (17)
C(31)	169 (23)	2203 (9)	3810 (17)	205 (36)	45 (20)	16 (40)	28 (5)	26 (15)	107 (19)
C(32)	584 (20)	2605 (8)	4458 (15)	180 (31)	10 (17)	50 (36)	21 (5)	-14 (13)	99 (17)
C(33)	9801 (22)	3052 (8)	4158 (15)	231 (36)	-40 (20)	100 (37)	28 (5)	-41 (14)	80 (15)
C(34)	8455 (20)	3100 (7)	3179 (14)	201 (32)	-10 (16)	64 (33)	17 (4)	-19 (11)	78 (14)

$h0l$ reflexions with l odd and $0k0$ reflexions with k odd.

The intensities were obtained from a crystal of approximate dimensions $0.17 \times 0.36 \times 0.44$ mm mounted on a Siemens AED single-crystal diffractometer (Mo $K\alpha$, Zr-filtered, θ - 2θ scan, scintillation counter with pulse-height discrimination). The unique b axis of the crystal (parallel to the shortest dimension of the crystal) was coincident with the polar φ axis of the goniostat. 3795 independent reflexions were measured in a hemisphere up to 2θ (Mo $K\alpha$) = 46° : 2752 of these, with $F_o^2 > 3\sigma(F_o^2)$, were used for the analysis. Correction for the shape anisotropy [$\mu(\text{Mo } K\alpha) = 48.9 \text{ cm}^{-1}$] was applied (Furnas, 1957; North, Phillips & Scott Matthews, 1968) with a procedure similar to that previously described (Spagna & Zambonelli, 1971). For this correction the variation in intensity of the conveniently intense axial reflexions 060 to $0,20,0$ was measured as a function of φ . Lorentz and polarization corrections were then applied.

The structure was solved by Patterson and Fourier methods. However it was not possible to distinguish the oxygen and carbon atoms of the 2,5-dimethylhex-3-yne-2,5-diol ligand, the electron density on the Fourier and difference maps in the region of the ligand being very diffuse. During and after the least-squares refinement, no indication arose for the identification of the oxygen atoms. For this reason only the scattering factor of carbon was used for the heavy atoms of the ligand molecule. The refinement was carried out by a 4×4 and 9×9 block-diagonal matrix least-squares method, the quantity minimized being $\sum w(|F_o| - |F_c|)^2$ with weights $w = 4F_o^2/\sigma(F_o^2)$. The initial refinement, with individual isotropic temperature factors assigned to all atoms, converged to an R of 0.094. A further refinement in which all atoms were allowed to vibrate anisotropically converged to $R = 0.054$. No attempt was made to include the contribution of the hydrogen atoms.

Atomic form factors given by Cromer & Mann (1968) were used. The effects of anomalous dispersion were included in the calculated structure factors and the values of $\Delta f'$ and $\Delta f''$ for Pt, Cl and P were those computed by Cromer (1965).

The positional and thermal parameters for all atoms are listed in Table 1, with the associated standard deviations as estimated from the inverse matrix. Relevant interatomic distances and angles are presented in Table 2.*

Discussion. The anion $[\text{PtCl}_3(\text{C}_8\text{H}_{14}\text{O}_2)]^-$ is a square-planar complex (Fig. 1). The 2,5-dimethylhex-3-yne-2,5-diol behaves as a monodentate ligand and is coordinated to the metal through its triple bond by a

* A list of structure amplitudes has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30139 (11 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Bond lengths and angles

Estimated standard deviations are given in parentheses. MP defines the midpoint of the acetylenic triple bond.

Anion			
Pt-Cl(1)	2.305 (6) Å	Cl(1)-Pt-Cl(2)	89.7 (2)°
Pt-Cl(2)	2.301 (5)	Cl(1)-Pt-Cl(3)	178.9 (3)
Pt-Cl(3)	2.298 (6)	Cl(1)-Pt-MP	90.6
Pt-MP	2.09	Cl(2)-Pt-Cl(3)	90.3 (2)
Pt-C(3)	2.25 (2)	Cl(2)-Pt-MP	176.9
Pt-C(4)	2.14 (3)	Cl(3)-Pt-MP	98.4
C(1)-C(2)	1.32 (5)	C(3)-Pt-C(4)	36 (1)
C(2)-C(3)	1.42 (5)	C(1)-C(2)-C(3)	104 (3)
C(3)-C(4)	1.34 (5)	C(1)-C(2)-C(7)	113 (5)
C(4)-C(5)	1.55 (5)	C(1)-C(2)-C(8)	110 (5)
C(5)-C(6)	1.50 (5)	C(7)-C(2)-C(3)	112 (3)
C(2)-C(7)	1.46 (8)	C(8)-C(2)-C(3)	108 (4)
C(2)-C(8)	1.50 (6)	C(2)-C(3)-C(4)	168 (3)
C(5)-C(9)	1.54 (6)	C(3)-C(4)-C(5)	156 (3)
C(5)-C(10)	1.47 (5)	C(4)-C(5)-C(6)	102 (3)
		C(4)-C(5)-C(9)	101 (3)
		C(4)-C(5)-C(10)	112 (3)
		C(6)-C(5)-C(9)	106 (3)
		C(6)-C(5)-C(10)	112 (3)
Cation, weighted mean values			
P-C	1.790 (8) Å	C-P-C	109.5 (7)°
C-C	1.399 (5)	P-C-C	118.9 (7)
		C-C-C	120.3 (5)

π -type bond. The other three coordination sites of the platinum atom are occupied by the chlorine atoms.

Pt, Cl(1), Cl(2) and Cl(3) lie almost exactly in a plane ($-9.103x + 4.165y + 3.127z + 0.132 = 0$, in terms of monoclinic coordinates). The midpoint of the acetylenic triple bond is 0.14 Å out of this plane and the triple bond makes with it an angle of 84.3° . The dihedral angle between the plane through Pt, C(3) and C(4) and the principal plane is 84.5° .

The three Pt-Cl bonds are equivalent with an average length of 2.301 (2) Å. This value is in good agreement

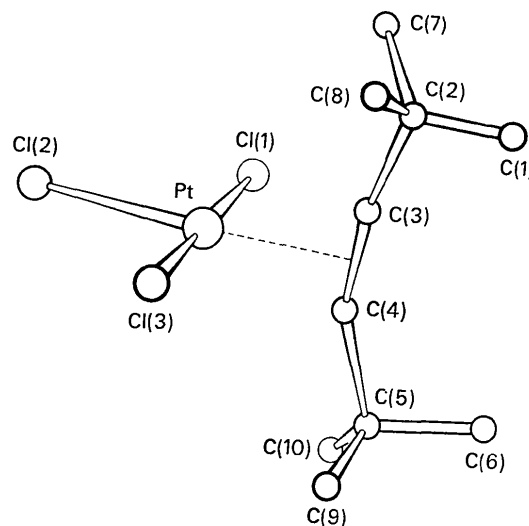


Fig. 1. Trichloro-(2,5-dimethylhex-3-yne-2,5-diol)platinate(II). A perspective view of the anionic complex.

with those found in the anion trichloro-(*cis*-but-2-ene-1,4-diol)platinate(II) (Colapietro & Zambonelli, 1971). The 2,5-dimethylhex-3-yne-2,5-diol does not appear to exercise a *trans* bond-lengthening effect when coordinated to platinum(II).

Any discussion about the geometry of the acetylenic ligand has no significance considering the low accuracy of the results. As previously mentioned the electron density on the Fourier and difference maps was very diffuse and it was not possible to distinguish the hydroxyl from the methyl groups bound to C(2) and C(5). The isotropic temperature factors of the terminal atoms of the ligand molecule reached very high values, giving no indication about the nature of the atoms. Any choice based on bond-length considerations is not meaningful. On the other hand no short contacts involving the hydroxyl groups, thus providing a criterion to find them, were observed. Any interaction between the hydroxyl groups of the ligand and the platinum or the chlorine atoms (Chatt *et al.*, 1963) may be excluded,

because none of the 'carbon' atoms bound to C(2) and C(5) lies sufficiently close to Pt, Cl(1), Cl(2) or Cl(3).

The geometry of the cation $P(C_6H_5)_4^+$ is almost regular.

The technical part of this work was performed by P. Mura.

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Refinement of the Crystal Structures of $Co_3V_2O_8$ and $Ni_3V_2O_8$

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Abstract. $Co_3V_2O_8$ and $Ni_3V_2O_8$, orthorhombic, *Cmca*, $Z=4$ with $a=6.030$ (4), $b=11.486$ (2), $c=8.312$ (5) Å, $D_{calc}=4.693$, $D_{exp}=4.70$ g cm⁻³ and $a=5.936$ (4), $b=11.420$ (6), $c=8.240$ (5) Å, $D_{calc}=4.828$, $D_{exp}=4.87$ g cm⁻³ respectively. Crystals of $Co_3V_2O_8$ were grown from the melt and $Ni_3V_2O_8$ from a KVO_3 flux. These structures, isotopic with that of $Mg_3V_2O_8$, are based upon a cubic closest packing of oxygen atoms with the cations in octahedral sites, showing average M–O bond lengths of 2.093 and 2.089 Å for M=Co, and 2.061 and 2.056 Å for M=Ni. V atoms lie on mirror planes and are tetrahedrally coordinated with mean V–O bond lengths of 1.732 and 1.736 Å for the Co and Ni salts, respectively. These structures differ from those proposed by Fuess, Bertaut, Pauthenent & Durif [*Acta Cryst.* (1970). **B29**, 2036] only in detail; as in $Mg_3V_2O_8$ and $Zn_3V_2O_8$, the longest V–O bond lengths involve the oxygen atom bonded to three cations and the vanadium ion.

Introduction. The intensities and cell dimensions were obtained from a crystal $0.20 \times 0.20 \times 0.15$ mm for $Co_3V_2O_8$ and a ground sphere with a radius of 0.25 mm for $Ni_3V_2O_8$ on a Syntex automatic diffractometer (Mo $K\alpha$, graphite-monochromated, θ - 2θ scan with

variable scan rate, scintillation counter with pulse height discrimination, a standard reflexion measured every fifty and background determined at both sides of each peak). Absorption and extinction corrections were applied.

Data were collected up to $2\theta=70^\circ$ for $Co_3V_2O_8$ and 50° for $Ni_3V_2O_8$ and yielded a total of 664 (507 above

Table 1. Atomic parameters with estimated standard errors

	x	y	z
(a) $Co_3V_2O_8$			
Co(1)	0	0	0
Co(2)	$\frac{1}{2}$	0.1329 (1)	$\frac{1}{2}$
V	0	0.3773 (1)	0.1204 (1)
O(1)	0	0.2503 (4)	0.2290 (6)
O(2)	0	0.0010 (4)	0.2447 (6)
O(3)	0.2703 (7)	0.1185 (2)	0.9983 (4)
(b) $Ni_3V_2O_8$			
Ni(1)	0	0	0
Ni(2)	$\frac{1}{2}$	0.13024 (3)	$\frac{1}{2}$
V	0	0.37623 (4)	0.11965 (7)
O(1)	0	0.2486 (2)	0.2309 (3)
O(2)	0	0.0013 (2)	0.2448 (3)
O(3)	0.26663 (3)	0.1189 (1)	0.0003 (3)