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Hexacarbonyl(triphenylphosphineaurio)vanadium

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Abstract. $C_{24}H_{15}AuO_6PV$, rhombohedral, $a = 11.088$ (10) Å, $\alpha = 75.4$ (2)°, $U = 1247.2$ Å³, $D_m = 1.80$, $D_c = 1.78$ Mg m⁻³, $F(000) = 512$, $Z = 2$, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 6.52$ mm⁻¹, space group $R\bar{3}$ from the successful structure determination. 888 independent reflections have been refined to $R = 0.059$. The molecule has crystallographically imposed 3 symmetry and the V atom is seven-coordinate and in a capped octahedral environment. The Au atom is in the capping position [V–Au 2.690 (3) Å] and the carbonyl groups are in the capped face [V–CO 2.002 (17) Å] and uncapped face [V–CO 1.932 (33) Å].

Introduction. There are very few examples of seven-coordinate molecules in which all the ligands are monodentate (Drew, 1977). Most of these have pentagonal-bipyramidal structures. However, in our view this was not likely to be the case for $V(CO)_6(AuPPh_3)$. This compound had been prepared many years ago (Kasenally, Nyholm, O'Brien & Stiddard, 1964) and contains one very bulky group, namely $AuPPh_3$, and we anticipated that this would need to keep well away from the other ligands. This could of course be achieved in a pentagonal bipyramid but a pentagonal girdle of five carbonyl groups seemed unlikely. In order to investigate further the structure of this molecule, and to continue our studies of seven-coordinate geometries, we have carried out a structure determination.

The crystals were prepared using the published method. Crystals of approximate size $0.3 \times 0.4 \times 0.5$ mm were mounted on a Stoe Stadi-2 diffractometer. 3378 reflections with a 2θ maximum of 45° were measured by ω scan with a scan speed of 30 s deg⁻¹

and a background count of 20 s. Of these, 888 independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. An absorption correction was applied (Stewart, 1972) but no extinction correction was made.

The positions of the Au and V atoms were obtained from the Patterson function and the positions of the remaining non-H atoms were obtained from Fourier maps. Atoms were refined anisotropically. H atoms were fixed in trigonal positions at 1.08 Å from the C atoms. Their thermal parameters were set equivalent to those of the C atoms to which they were bonded. The final R value was 0.059. Calculations were carried out using the *SHELX 76* system (Sheldrick, 1976) at the University of Manchester Computer Centre. Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates ($\times 10^5$ for Au, $\times 10^4$ for other atoms) and isotropic thermal parameters ($\times 10^3$) with *e.s.d.*'s in parentheses

	x	y	z	$U(\text{Å}^2)$
Au(1)	24800 (1)	24800 (1)	24800 (1)	61 (1)
V(1)	1337 (2)	1337 (2)	1337 (2)	72 (3)
P(1)	3439 (2)	3439 (2)	3439 (2)	52 (3)
C(1)	4768 (11)	4117 (11)	2380 (12)	54 (15)
C(2)	5522 (15)	3457 (13)	1489 (14)	84 (20)
C(3)	6599 (16)	3876 (17)	674 (16)	100 (24)
C(4)	6885 (15)	4975 (18)	838 (17)	97 (23)
C(5)	6144 (16)	5619 (18)	1699 (16)	88 (25)
C(6)	5048 (15)	5217 (16)	2503 (15)	76 (22)
C(7)	3176 (16)	1362 (12)	571 (13)	66 (18)
O(7)	4190 (13)	1371 (11)	18 (10)	99 (17)
C(8)	1087 (28)	1851 (32)	-401 (30)	148 (57)
O(8)	928 (24)	2222 (28)	1418 (18)	217 (50)

Table 2. Bond distances (Å) and angles (°)

Au—V	2.690 (3)	C(1)—C(2)	1.358 (20)
Au—P	2.260 (3)	C(1)—C(6)	1.374 (25)
Au...C(7)	2.573 (16)	C(2)—C(3)	1.403 (23)
V—C(7)	2.002 (17)	C(3)—C(4)	1.400 (32)
V—C(8)	1.932 (33)	C(4)—C(5)	1.324 (26)
P—C(1)	1.829 (13)	C(5)—C(6)	1.414 (23)
		C(7)—O(7)	1.137 (21)
		C(8)—O(8)	1.140 (39)
V—Au—P	180.0	P—C(1)—C(2)	117.3 (11)
C(7)—Au—C(7')	75.0 (5)	P—C(1)—C(6)	122.2 (11)
Au—V—C(7)	64.6 (6)	C(6)—C(1)—C(2)	120.4 (11)
Au—V—C(8)	126.8 (11)	C(1)—C(2)—C(3)	121.5 (16)
C(7)—V—C(8)	85.3 (10)	C(2)—C(3)—C(4)	117.4 (16)
C(7)—V—C(7')	102.9 (6)	C(3)—C(4)—C(5)	120.7 (16)
C(7)—V—C(8')	82.6 (11)	C(4)—C(5)—C(6)	121.9 (20)
C(7)—V—C(8'')	168.5 (12)	C(1)—C(6)—C(5)	118.0 (15)
C(8)—V—C(8')	87.8 (4)	V—C(7)—O(7)	173.0 (16)
Au—P—C(1)	113.9 (5)	V—C(8)—O(8)	175.9 (34)
C(1)—P—C(1')	104.7 (6)		

Symmetry code: (') y, z, x ; (") z, x, y .

The weighting scheme, $w = [\sigma^2(F) + 0.003F^2]^{-1}$ where $\sigma(F)$ is taken from counting statistics, was chosen to give similar values of $w\Delta^2$ over ranges of $\sin \theta/\lambda$ and F_o . The difference Fourier maps showed no significant peaks. Zero-weighted unobserved reflections showed no serious discrepancies. Atomic coordinates are given in Table 1 and molecular dimensions in Table 2.*

Discussion. The structure of $V(CO)_6(AuPPh_3)$ is shown in Fig. 1. The molecule has crystallographically imposed 3 symmetry with the Au and V atoms on the axis. The V atom is seven-coordinate with a capped octahedral environment. The Au atom is in the capping position with V—Au 2.690 (3) Å and the six carbonyls are in the capped and uncapped faces.

According to the Cambridge Data Centre files there is no other structure which contains an Au—V bond. However, the bond length of 2.690 (3) Å seems appropriate for a single bond. The V—C(7) and V—C(8) bond lengths are 2.002 (17) and 1.932 (33) Å respectively and though not too much significance should be read into the difference, the longer bond is to C(7) which is in the crowded capped face of the capped octahedron next to the Au atom.

The capped octahedron has rather different dimensions from those which are usually observed. Thus the Au—V—C(7) and C(7)—V—C(7') angles are 64.6 (6) and 102.9 (6)° compared to the more usual values of 74.1 and 112.8° (Drew, 1977). Thus the capping Au atom has made less impact than is usually the case

*Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36214 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

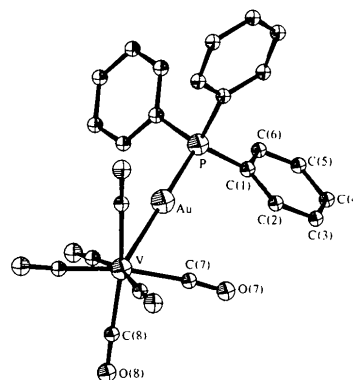


Fig. 1. A perspective view of the molecule.

upon the capped face and the three carbonyls are spaced out from their octahedral positions by just over half as much as usual. Clearly this is caused by the long Au—V bond and the fact that the P atoms and the benzene rings are over 4 Å away from the capped-face carbonyls. It is interesting that the thermal parameters of the carbonyls are much larger than those for the benzene rings. It is possible that there is some disorder in their position though we were not able to quantify it. The C(1)—P...V—C(7) torsion angle is 27.3 (1)° indicating that the benzene-ring atoms need not be staggered with respect to the carbonyls in the capped face. The benzene-ring planes make an angle of 35.5 (1)° with the V...P—C(1) plane. The closest contact between a phenyl-ring atom and a carbonyl is 3.40 Å for H(1)...C(7).

The molecule has almost C_{3v} symmetry as far as the coordination sphere is concerned, with *cis* angles between carbonyls C(7) and C(8) being 85.3 (10) and 82.6 (11)° rather than being equivalent. There are no non-bonded contacts less than the sum of the van der Waals radii, the shortest involving non-H atoms being O(7)...C(5) 3.39 Å (symmetry operation: $1 - x, 1 - y, -z$).

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