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Disorder in the lactato group of (lactato-*O,O'*)bis(triphenylphosphine-*P*)silver(I) corroborated by ^{31}P two-dimensional CPCOSY NMR

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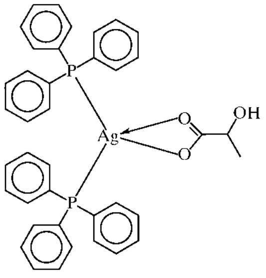
The Ag atom in the title compound, $[Ag(C_3H_5O_3)(C_{18}H_{15}P)_2]$, is bonded to the P atoms of two triphenylphosphine ligands and to the two O atoms of the carboxyl unit of the lactato group in a distorted tetrahedral environment. The lactato anion is disordered in the methyl and hydroxyl groups; the 1:1 disorder is corroborated by two-dimensional ^{31}P CPCOSY (cross-polarization, correlation spectroscopy) NMR.

Comment

The reaction of silver acetate and triphenylphosphine in ethanol produces 1:1 and 1:2 adducts, and both adducts crystallize with one or more water/ethanol molecules (Hanna & Ng, 1999; Ng & Othman, 1995, 1997). Silver trifluoroacetate yields only the anhydrous 1:2 adduct (Ng, 1998), as does the present lactate, (lactato-*O,O'*)bis(triphenylphosphine-*P*)silver(I), (I). In (I), the Ag atom shows tetrahedral coordination [Ag—P = 2.4345 (9) and 2.4671 (9) Å, and Ag—O = 2.425 (3) and 2.508 (4) Å], but the geometry is distorted owing to the small bite of the carboxyl group [O—Ag—O = 51.3 (1)°]. The geometry is similar to that found in the analogous bis(triphenylphosphine) complexes of acetate and trifluoroacetate.



(I)

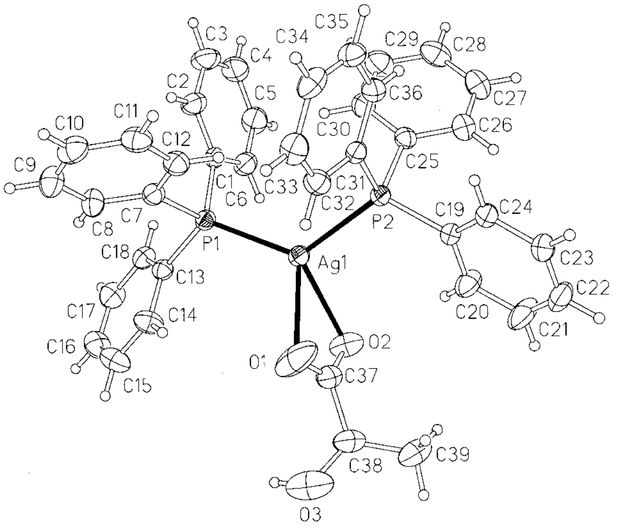


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level. The disorder is not shown. H atoms are drawn as spheres of arbitrary radii.

The solid-state NMR spectral characterization of the title compound was undertaken with ^{13}C CPMAS (cross-polarization, magic-angle-spinning), one-dimensional ^{31}P CPMAS and two-dimensional ^{31}P CPCOSY (cross-polarization, correlation spectroscopy) techniques. The ^{13}C CPMAS NMR confirmed the lactate coordination, with resonances being observed at 24.2, 70.3 and 183.1 p.p.m. These resonances are assigned to the $-CH_3$, $-CH(OH)$ and $-CO_2$ groups, respectively. The unit cell has only one independent molecule, but the molecule exhibits disorder with respect to the positioning of the $-CH_3$ and $-OH$ groups. The ^{13}C NMR chemical shifts are insensitive to this disorder, however, so that only one methyl signal is observed. On the other hand, the ^{31}P NMR chemical shifts are much more sensitive to such structural differences. In the ^{31}P CPMAS spectrum, both orientations of the CH_3/OH groups are clearly resolved to be (approximately) equally distributed (*i.e.* 1:1) between the two orientations. The much larger ^{31}P chemical shift anisotropy and the greater sensitivity of the σ_{11}, σ_{22} and σ_{33} shift tensorial elements with respect to long-range metal coordination and geometry make this nucleus more diagnostic in the study of such disorder than its ^{13}C counterparts. The one-dimensional ^{31}P CPMAS spectrum is a complex overlap of four doublet-of-doublets (*i.e.* 16 resonances) that can only be properly analyzed in a two-dimensional ^{31}P CPCOSY experiment. The one-bond $^1J_{Ag-P}$ coupling constants exhibit virtually no variation (within experimental error) from this disorder, with orientation 1 yielding 478 and 390 Hz, and orientation 2 yielding 471 and 389 Hz (see *Experimental*).

The structure of [silver bis(triphenylphosphine)-acetate]$\cdot 0.5H_2O \cdot 0.75CH_3CH_2OH$ is disordered (Hanna & Ng, 1999), but the disorder concerns only the lattice ethanol, which is hydrogen bonded to the lattice water molecule. The disorder is not noted in its ^{31}P CPMAS.

The invariate behaviour of the $^1J_{Ag-P}$ coupling constants of the lactate in (I) suggests that the bond angles and distances of the P_2AgO_2 core, and the phenyl ring twist of each triphenylphosphine entity, are largely unperturbed by the different orientations defining this disorder. However, the spread of ^{31}P chemical shifts from the two P sites in each molecule is unambiguously different for each orientation adopted by the lactate group. Orientation 1 yields a greater dispersion of ^{31}P chemical shifts, with values of 18.5 and 12.9 p.p.m. being obtained, whereas the shifts defining orientation 2 (16.6 and 13.6 p.p.m.) are much closer.

Experimental

Silver(I) lactate and triphenylphosphine (1:1 molar ratio) were dissolved in a small volume of ethanol. Slow cooling of the filtered solution yielded the title adduct, (I), as large crystals. The solid-state ^{31}P NMR spectrum was interpreted in terms of two orientations of the anion. Spectroscopic data for orientation 1 (δ, p.p.m.): 18.5 [$^1J_{Ag-P}$ = 478 Hz, $^2J_{P-P}$ = 144 Hz]; 12.9 [$^1J_{Ag-P}$ = 390 Hz, $^2J_{P-P}$ = 144 Hz]; orientation 2 (δ, p.p.m.): 16.6 [$^1J_{Ag-P}$ = 471 Hz, $^2J_{P-P}$ = 144 Hz]; 13.6 [$^1J_{Ag-P}$ = 478 Hz, $^2J_{P-P}$ = 144 Hz].

Crystal data

$[Ag(C_3H_5O_3)(C_{18}H_{15}P)_2]$
$M_r = 721.48$
Triclinic, $P\overline{1}$
$a = 12.5745$ (1) Å
$b = 12.8844$ (1) Å
$c = 13.0438$ (1) Å
$\alpha = 73.967$ (1)°
$\beta = 66.242$ (1)°
$\gamma = 62.598$ (1)°
$V = 1706.43$ (2) Å^3

$Z = 2$
$D_x = 1.404$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8418 reflections
$\theta = 1.79$–29.25°
$\mu = 0.721$ mm^{-1}
$T = 298$ (2) K
Block, colourless
0.43 × 0.38 × 0.15 mm

Data collection

Siemens CCD area-detector diffractometer
Frames ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.727$, $T_{max} = 0.875$
8775 measured reflections

5792 independent reflections
5263 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25°$
$h = -10 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.107$
$S = 1.091$
5792 reflections
413 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 1.5612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.592$ e Å^{-3}
$\Delta\rho_{min} = -0.782$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.013 (1)

Table 1
Selected geometric parameters (Å, °).

Ag1—P1	2.4345 (9)	Ag1—O1	2.508 (4)
Ag1—P2	2.4671 (9)	Ag1—O2	2.425 (3)
P1—Ag1—P2	126.15 (3)	P2—Ag1—O1	109.7 (2)
P1—Ag1—O1	114.6 (1)	P2—Ag1—O2	104.7 (1)
P1—Ag1—O2	126.5 (1)	O1—Ag1—O2	51.3 (1)

The methyl and hydroxyl groups on the C38 atom are disordered over two positions and were refined as two $(CH_3)(OH)CH$- groups sharing a common C38 atom, subject to C—C = 1.54 (1), C—O = 1.45 (1), C···C = 2.52 (2) and C···O = 2.44 (2) Å. The displacement parameters for the unprimed and primed atoms were set to be equal.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1054). Services for accessing these data are described at the back of the journal.

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