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Dicyclohexylammonium 2,4-dichlorophenoxyacetate and (2,4-dichlorophenoxyacetato-*O,O'*)bis(triphenylphosphine-*P*)silver(I)

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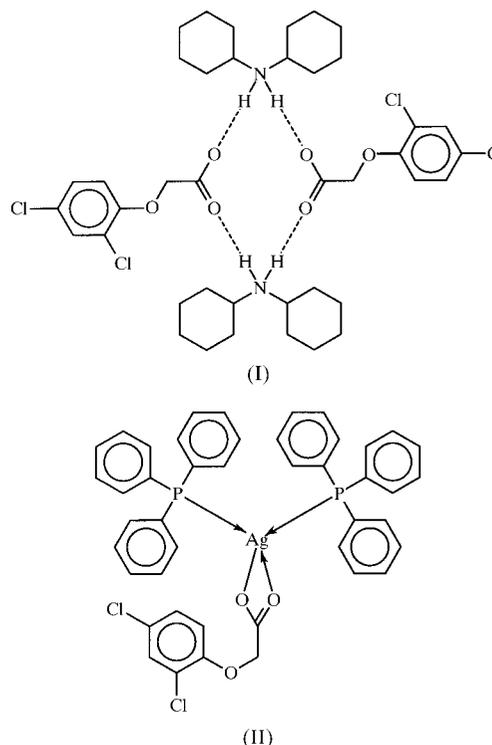
Data validation number: IUC0000157

The monoclinic cell of dicyclohexylammonium 2,4-dichlorophenoxyacetate contains four $C_{12}H_{24}N^+ \cdot C_5H_8Cl_2O_3^-$ ion pairs. The ammonium N atom is hydrogen bonded to the oxygen ends of two carboxyl groups to form a 12-membered $O-C-O \cdots HNH \cdots O-C-O \cdots HNH$ ring. In (2,4-dichlorophenoxyacetato)bis(triphenylphosphine)silver(I), $[Ag(C_8H_5Cl_2O_3)(C_{18}H_{15}P)_2]$, the carboxyl CO_2 unit chelates to the Ag atom in an anisobidentate manner [$Ag-O = 2.436(2)$ and $2.517(2)$ Å]; the Ag atom shows distorted tetrahedral geometry.

Comment

Dimeric 2,4-dichlorophenoxyacetic acid [$O \cdots O = 2.632(6)$ Å; Smith *et al.*, 1976] is a potent herbicide (Que Hee & Sutherland, 1981). The acid cocrystallizes with 4-aminobenzoic acid (Lynch *et al.*, 1992) and with 2-aminopyrimidine (Lynch *et al.*, 1994), and its anion has been characterized as the zinc (Kennard *et al.*, 1982), potassium (Kennard *et al.*, 1983), silver (Mak *et al.*, 1988) and copper (Dendrinou-Samara *et al.*, 1996) salts. The only ammonium salt of the acid that has been examined appears to be the 3-hydroxypyridinium derivative, which adopts a chain structure in which the anions are linked by hydrogen bonds ($N \cdots O = 2.60$ and $O \cdots O = 2.55$ Å; Byriell *et al.*, 1992). The study on the present dicyclohexylammonium salt, (I), continues studies of dicyclohexylammonium salts of monocarboxylic acids. Dicyclohexylammonium trifluoroacetate crystallizes as linear hydrogen-bonded chains [$N \cdots O =$

$2.785(2)$ and $2.794(2)$ Å; Ng *et al.*, 1999], but this architecture is not common as several other dicyclohexylammonium monocarboxylates pack as dimeric ion pairs across a centre of



symmetry. Such an architecture is observed for the *O*-(*N,N*-dimethylmonothiocarbamoyl)acetate [$N \cdots O = 2.706(4)$ and $2.750(3)$ Å], *N*-phthaloylglycinate [$N \cdots O = 2.733(5)$ and $2.783(5)$ Å; Ng, 1995], bis(*N,N*-dimethyldithiocarbamoyl)acetate [$N \cdots O = 2.701(3)$ and $2.796(3)$ Å; $2.698(3)$ and $2.837(3)$ Å; Ng, 1996], *N,N*-dicyclohexyldithiocarbamoylacetate [$N \cdots O = 2.706(2)$ and $2.757(2)$ Å; Ng, 1997] and 3-oxapentamethylenedithiocarbamoylacetate [$N \cdots O = 2.732(4)$ and $2.738(4)$ Å; Ng & Hook, 1999]. As the substituted acetate group carries bulky substituents, steric effects probably contribute to this type of dimer formation. This arrangement is also found in the 2,4-dichlorophenoxyacetate [$N \cdots O = 2.751(3)$ and $2.784(3)$ Å]. The carbon–oxygen distances in the carboxyl $-CO_2$ end [$C-O = 1.224(2)$ and $1.238(2)$ Å] indicate delocalization of the negative charge. At the ether linkage, the $C_{alkyl}-O$ distance [$C-O = 1.421(4)$ Å] exceeds the $C_{aryl}-O$ distance [$C-O = 1.356(4)$ Å]. Bond dimensions in the anion are not much different from those found in the parent acid [$C-O_{carboxyl} = 1.217(6)$ and $1.304(5)$ Å; $C_{alkyl}-O = 1.423(5)$, $C_{aryl}-O = 1.365(5)$ Å; Smith *et al.*, 1976]. In the parent acid as well as in the dicyclohexylammonium salt, the angle at the ether linkage is nearly 120° . The bond dimensions of the ether linkage in the acid and in the salt are in agreement with the results ($C_{alkyl}-O = 1.407$, $C_{aryl}-O = 1.371$ Å and $C-O-C = 119.4^\circ$) of molecular mechanics calculations on the monomeric acid computed with the *MM3+* basis set (Hypercube Inc., 1995). The computations suggest a planar structure as the most stable conformation; on the other hand, the carboxyl unit is twisted

by 85.2° with respect to the aromatic ring in the acid and by 80.8 (3)° in the salt. The synclinal conformation of 2,4-dichlorophenoxyacetic acid appears to be a feature that is not usually found in other phenoxyacetic acids or in metal phenoxyacetates (Mak *et al.*, 1988) such as zinc 2,4-dichlorophenoxyacetate (Kennard *et al.*, 1982) and potassium 2,4-dichlorophenoxyacetate (Kennard *et al.*, 1983).

The silver 2,4-dichlorophenoxyacetate dimer, for which only partial structural details are reported, displays a zigzag motif that is derived through carboxylate bridging of the two independent molecules, and both Ag atoms are two-coordinate. The compound is isomorphous and isostructural with silver 2-methyl-4-chlorophenoxyacetate [Ag—O = 2.185 (3)–2.217 (3) Å], whose full structural details are reported. As the dihedral angles between the carboxyl and the aromatic planes in the latter compound are 15 and 18°, both individual monomers are almost planar (Mak *et al.*, 1988). (2,4-Dichlorophenoxyacetato)bis(triphenylphosphine)silver, (II), shows a twist [dihedral angle = 65.1 (1)°] that is comparable with that found in the dicyclohexylammonium salt. The chain motif of the silver salt is disrupted upon coordination by the two phosphine-donor ligands, and two weaker silver–oxygen bonds are formed instead [Ag—O = 2.435 (2) and 2.516 (2) Å]. The distorted tetrahedral geometry of silver in this adduct is similar to those found in a number of 1:2 adducts of silver carboxylates with triphenylphosphine such as the acetate (Ng & Othman, 1997), trifluoroacetate (Ng, 1998) and lactate (Hanna & Ng, 2000).

Of the two triphenylphosphine ligands, one is disordered in two of phenyl rings. The C1–C6/C1'–C7' pair of rings are twisted by 42 (1)°, and the C7–C12/C7'–C12' pair by 33 (1)°. The disorder is corroborated by the CP/MAS spectral values: the $^1J(\text{Ag–P})$ coupling constants of the ordered and disordered phosphorus sites are significantly different. The line-widths of the NMR signals constitute the basis for assigning the ordered/disordered sites; the ordered phosphorus signal yields $^1J(^{107}\text{Ag–}^{31}\text{P})$ and $^1J(^{109}\text{Ag–}^{31}\text{P})$ couplings that are clearly resolved, whereas the disordered phosphorus signal is Lorentzian broaden so that these couplings cannot be resolved. The silver–phosphorus_{disordered} distance [2.4073 (8) Å] is statistically shorter than the silver–phosphorus_{ordered} distance [2.4753 (8) Å].

Experimental

Dicyclohexylamine, dissolved in a small volume of ethanol, was added to an ethanol solution of 2,4-dichlorophenoxyacetic acid (1:1 molar ratio of reactants). Ethanol was added to dissolve the ammonium carboxylate that precipitated from solution, and the mixture was heated until most had dissolved completely; the filtered solution afforded long colourless crystals when it was cooled. Solid-state cross-polarization/magic angle-spinning (CP/MAS) ^{13}C NMR: δ = 172.3 (–CO₂); 154.3, 129.8, 114.1 (–C₆H₃Cl₂); 68.0 (–CH₂–O–); 54.6, 51.4, 31.4, 29.8, 28.1, 26.2 p.p.m. (cyclo-C₆H₁₁). Equimolar quantities of aqueous sodium 2,4-dichlorophenoxyacetate and silver nitrate were mixed to afford an immediate white precipitate of silver 2,4-dichlorophenoxyacetate, which was collected, washed with water, and

then air dried. The silver salt and triphenylphosphine (1:2 molar ratio) were heated in a small volume of ethanol until the reactants dissolved completely; slow cooling of the filtered solution yielded faint tan-colored crystals of the 1:2 complex. ^{13}C NMR: δ = 173.9 (–CO₂); 155.6, 135.4–130.1, 116.4 (–C₆H₃Cl₂ overlapped with –C₆H₅); 70.3 p.p.m. (–CH₂–O). CP/MAS ^{31}P NMR for the ordered triphenylphosphine ligand: δ = 20.8±0.1 p.p.m., $^1J(\text{Ag–P})$ = 508±4 Hz, $^2J(\text{P–P})$ = 140±4 Hz. CP/MAS ^{31}P NMR for the disordered triphenylphosphine ligand: δ = 15.9±0.1 p.p.m., $^1J(\text{Ag–P})$ = 383±4 Hz, $^2J(\text{P–P})$ = 140±4 Hz.

Compound (I)

Crystal data

$\text{C}_{12}\text{H}_{24}\text{N}^+\cdot\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3^-$
 M_r = 402.34
 Monoclinic, $P2_1/c$
 a = 13.3847 (1) Å
 b = 18.2966 (3) Å
 c = 8.9780 (1) Å
 β = 105.296 (1)°
 V = 2120.78 (4) Å³
 Z = 4

D_x = 1.260 Mg m^{–3}
 Mo $K\alpha$ radiation
 Cell parameters from 6107 reflections
 θ = 2.73–28.37°
 μ = 0.325 mm^{–1}
 T = 298 (2) K
 Parallelepiped, colourless
 0.48 × 0.42 × 0.28 mm

Data collection

Siemens CCD area-detector diffractometer
 w scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 T_{min} = 0.860, T_{max} = 0.915
 11 531 measured reflections
 3737 independent reflections

2447 reflections with $I > 2\sigma(I)$
 R_{int} = 0.059
 θ_{max} = 25°
 h = –15 → 15
 k = –21 → 11
 l = –10 → 10
 50 standard frames at start and end
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.063
 $wR(F^2)$ = 0.198
 S = 1.064
 3737 reflections
 244 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0975P)^2 + 0.5146P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.014 (2)

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1A \cdots O1	0.95 (4)	1.85 (4)	2.784 (3)	169 (3)
N1—H1B \cdots O2 ⁱ	0.86 (4)	1.90 (4)	2.751 (3)	171 (3)

Symmetry code: (i) $-x, 1 - y, -z$.

Compound (II)

Crystal data

$[\text{Ag}(\text{C}_8\text{H}_5\text{Cl}_2\text{O}_3)(\text{C}_{18}\text{H}_{15}\text{P}_2)]$
 M_r = 852.43
 Monoclinic, $P2_1/c$
 a = 13.4500 (2) Å
 b = 25.8202 (4) Å
 c = 11.7071 (2) Å
 β = 96.790 (1)°
 V = 4037.2 (1) Å³
 Z = 4

D_x = 1.402 Mg m^{–3}
 Mo $K\alpha$ radiation
 Cell parameters from 7909 reflections
 θ = 2.82–28.38°
 μ = 0.749 mm^{–1}
 T = 298 (2) K
 Parallelepiped, colourless
 0.42 × 0.38 × 0.28 mm

Data collection

Siemens CCD area-detector diffractometer	5520 reflections with $I > 2\sigma(I)$
w scans	$R_{\text{int}} = 0.066$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 25^\circ$
$T_{\text{min}} = 0.744$, $T_{\text{max}} = 0.818$	$h = -15 \rightarrow 15$
22 253 measured reflections	$k = -26 \rightarrow 30$
7085 independent reflections	$l = -13 \rightarrow 13$
	50 frames from start to end
	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0580P)^2]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.972$	$(\Delta/\sigma)_{\text{max}} = 0.001$
7085 reflections	$\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
531 parameters	$\Delta\rho_{\text{min}} = -0.63 \text{ e } \text{\AA}^{-3}$

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Ag1—O1	2.435 (2)	Ag1—P1	2.4073 (8)
Ag1—O2	2.516 (2)	Ag1—P2	2.4753 (8)
O1—Ag1—O2	52.9 (1)	O2—Ag1—P1	118.2 (1)
O1—Ag1—O1	129.6 (1)	O2—Ag1—P2	102.7 (1)
O1—Ag1—P2	101.5 (1)	P1—Ag1—P2	127.0 (1)

In (II), two of the phenyl rings of one of the triphenylphosphine ligands are disordered, and each was refined as two regular hexagons; an ISOR 0.02 instruction was used on all the disordered atoms. The P—C_{ipso} distances were restrained by a SADI 0.01 instruction, as were the four P—C_{ortho} distances.

For both compounds, data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

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