Acta Cryst. (1999). C**55**, 539-541

Potassium methoxyacetate tetrahydrate†

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(*Received 15 April 1998; accepted 4 November 1998*)

Abstract

The title complex, $K^+\cdot CH_3OCH_2COO^-\cdot 4H_2O$, forms a network in which K atoms are nine-coordinate, bonding to a carboxylate O atom and the ether O atom of each of two different methoxyacetate groups, to both carboxylate O atoms of a third group, to a single carboxylate O atom of a fourth group and also to two water molecules. Additional water molecules are involved in hydrogen bonding to the polymeric complex.

Comment

The discovery that salts of 2-[2-{2-(methoxy)ethoxy}-ethoxy]acetate (MEEA) are liquids at room temperature (Apblett, Long *et al.*, 1994; Apblett *et al.*, 1995) and are useful reagents for the synthesis of metal–oxide ceramics (Apblett *et al.*, 1997*a*,*b*; Apblett, Breen & Walker, 1998; Apblett, Georgieva *et al.*, 1998) has prompted the structural investigation of simpler ether-containing carboxylates that are solids. It is expected that the structural and spectroscopic characterization of salts of methoxyacetate will provide correlations which will be useful for understanding the behavior of the MEEA salts. Indeed, the initial investigation of the MEEA salts was initiated by earlier success with methoxyacetates as precursors for barium titanate (Apblett, Georgieva & Raygoza-Maceda, 1994). To this end, potassium methoxyacetate tetrahydrate, (I), has been synthesised, and its crystal structure is reported here. The molecular structure of (I) is shown in Fig. 1.

Each K atom in (I) is nine-coordinate [mean K—O 2.968 (3) Å], being bound to two versions of O10, to a carboxylate O atom of one methoxyacetate group, to the two carboxylate O atoms of a second methoxyacetate group, and to the single carboxylate O atoms and the ether O atoms of a third and fourth methoxyacetate group. The four linkages to the third and fourth methoxyacetate groups serve to bridge two K atoms [K···K 3.856 (2) Å]. Each K atom has threefold bridging (water atom O10, and the carboxylate O atoms of two methoxyacetate groups) to two additional K neighbors [K···K 4.331 (2) Å]. The K atoms are linked together in sheets, and hydrogen-bonding interactions involving O11, O12 and O13 serve to link these sheets together (Fig. 2).

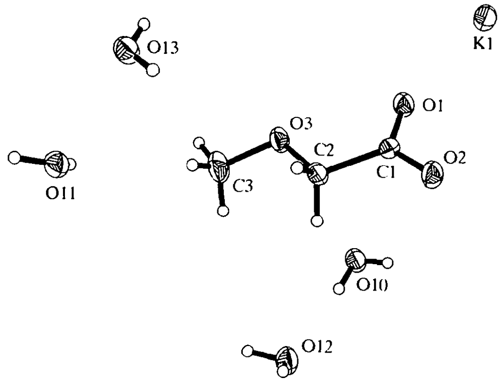

Fig. 1. The molecular structure of potassium methoxyacetate tetrahydrate, showing the atom-numbering scheme. Displacement ellipsoids are shown at 50% probability and H atoms are drawn as spheres of arbitrary radii.

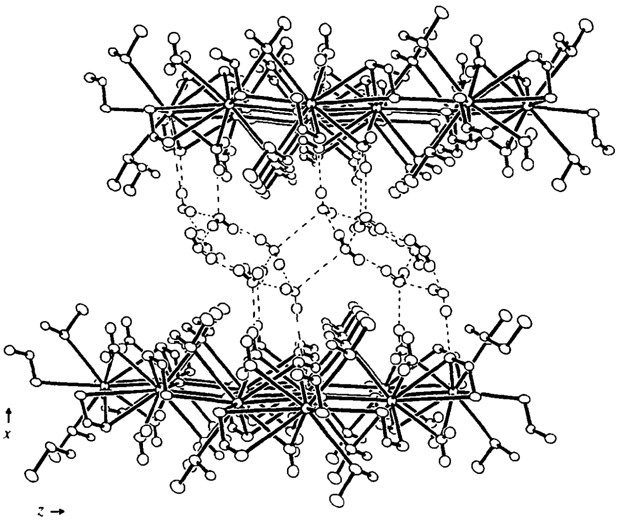

Fig. 2. Packing diagram of (I), viewed along [010]. Hydrogen bonds are indicated by dashed lines. Displacement ellipsoids are shown at 50% probability and H atoms are drawn as spheres of arbitrary radii.

The arrangement of the methoxyacetate ligand in the potassium salt differs remarkably from that reported previously for the salts $M(O_2CCH_2OCH_3)_2\cdot 2H_2O$ [M = Cu (Prout *et al.*, 1968) or Ni (Prout, Walker & Rosotti, 1971)] and $Cu(O_2CCH_2OCH_3)_2(pyridine)_2$ (Prout, Barrow & Rosotti, 1971), in which the ligand also forms five-membered chelate rings but in which the carboxylates are monodentate rather than bridging. The only other reported structure for a methoxyacetate complex is $Cu(CO_2CH_2OCH_3)_2(imidazole)_4$, in which the ligand is monodentate, coordinating through only one carboxylate O atom (Prout, Allison & Rosotti, 1971).

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† Systematic name: potassium 3-oxabutanoate tetrahydrate.

The bond distances and angles of the methoxyactetate ligand in the potassium salt are comparable to those of the transition metal chelates, with the exception of the C$\overset{\cdots}{-}$O distances of the carboxylate, which are nearly equal in the potassium complex as a result of the more symmetrical bridging mode of coordination, leading to complete delocalization of the double bond. In the diaquabis(methoxyacetato)nickel(II) and diaquabis(methoxyacetato)copper(II) complexes, the corresponding C$\overset{\cdots}{-}$O bond distances of the carboxylate show a significantly larger variation and are also, on average, somewhat shorter than the distances in the potassium salt (*e.g.* 1.23 and 1.24 Å, respectively, *versus* 1.266 Å). Despite the differences in coordination modes, there is little variation in the carboxylate O—C—O angle, although it is largest for the potassium complex, at 125.4°, *versus* 125.2 and 124.7° for the nickel and copper diaquabis(methoxyacetate) complexes, respectively.

Experimental

Potassium methoxyacetate tetrahydrate was prepared by neutralizing a solution of potassium carbonate (1.38 g, 10.0 mmol) by slow addition to a solution of methoxyacetic acid (1.81 g, 20.1 mmol) in 20 ml of water. After evolution of carbon dioxide had ceased, the water was evaporated with a stream of air. After being concentrated to *ca* 3 ml, the liquid phase rapidly crystallized to yield colorless rectangular crystals of (I).

Crystal data

$K^+\cdot C_3H_5O_3^-\cdot 4H_2O$
$M_r = 200.2$
Monoclinic
$P2_1/c$
$a = 12.189\,(6)$ Å
$b = 6.640\,(3)$ Å
$c = 12.393\,(5)$ Å
$\beta = 105.36\,(2)°$
$V = 967.20\,(8)$ Å^3
$Z = 4$
$D_x = 1.371$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 43 reflections
$\theta = 5.20$–$12.59°$
$\mu = 0.545$ mm^{-1}
$T = 301$ K
Rhombohedral
$0.2 \times 0.2 \times 0.2$ mm
Colorless

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3688 measured reflections
2826 independent reflections
1808 reflections with $F > 4.5\sigma(F)$

$R_{\rm int} = 0.057$
$\theta_{\rm max} = 30°$
$h = -1 \rightarrow 17$
$k = -9 \rightarrow 1$
$l = -17 \rightarrow 16$
3 standard reflections every 97 reflections intensity decay: negligible

Refinement

Refinement on F
$R = 0.049$
$wR = 0.072$
$S = 1.42$
2826 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å)*

K1—O1	3.382 (3)	K1—O10$^{\rm iv}$	2.898 (3)
K1—O2	3.104 (2)	K1—O10$^{\rm iii}$	2.842 (2)
K1—O1$^{\rm i}$	2.863 (2)	O1—C1	1.263 (3)
K1—O3$^{\rm i}$	2.920 (2)	O2—C1	1.269 (3)
K1—O2$^{\rm ii}$	2.798 (2)	O3—C2	1.425 (3)
K1—O1$^{\rm iii}$	3.045 (3)	O3—C3	1.422 (4)
K1—O3$^{\rm iii}$	2.865 (3)	C1—C2	1.530 (3)

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $-x, -y, 2-z$.

A variable scan rate was used in a $\theta/2\theta$-scan mode, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$, to a maximum 2θ value of 50°. Refinement was completed using full-matrix least-squares methods. Extinction was refined but was minimal.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *XP* (Siemens, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1073). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 541–543

Chloro(diethyl dithiophosphato-*S*,*S*′)(triphenylphosphine-*P*)palladium(II)

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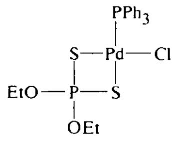
(*Received 18 May 1998; accepted 12 November 1998*)

Abstract

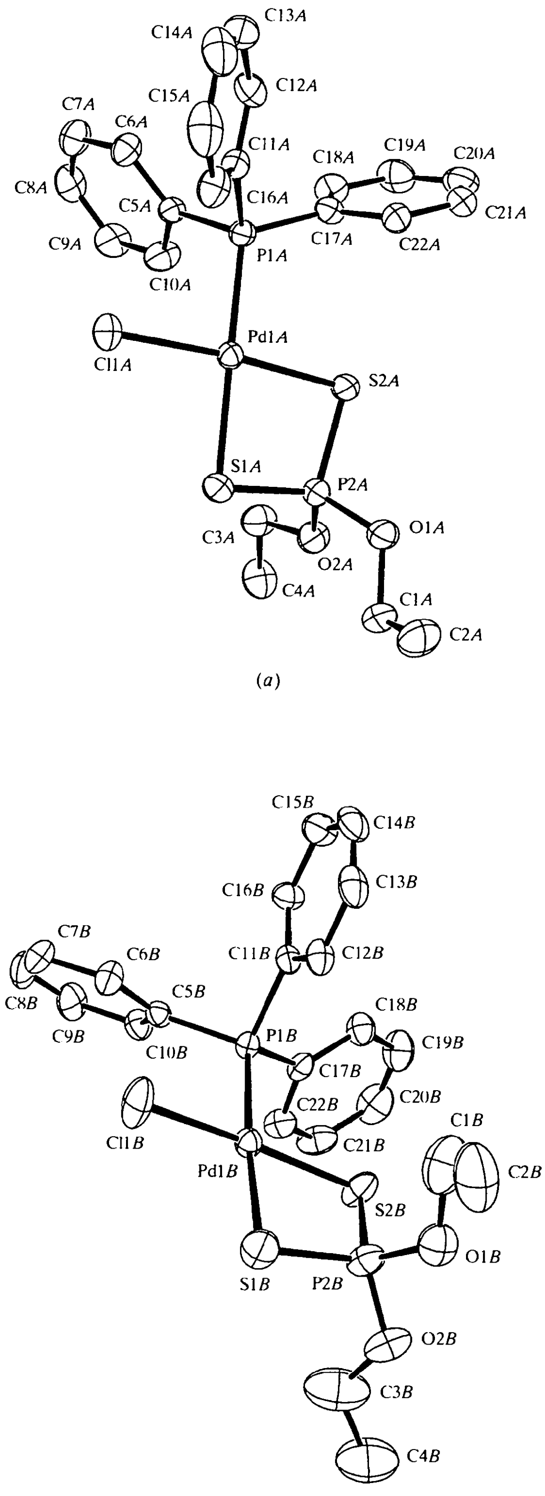
The structure of the title compound, $[PdCl(C_4H_{10}O_2PS_2)(C_{18}H_{15}P)]$, is reported. There are two independent molecules in the asymmetric unit. The coordination around the Pd atom in each molecule is distorted square planar. Both molecules have nearly the same conformation, except for the orientation of the ethyl groups on the dithiophosphate ligand. Bond lengths and angles are typical of related Pd and Pt complexes.

Comment

The chemistry of palladium(II) and platinum(II) with dithio ligands, such as xanthate, dithiocarbamate and dithiophosphates, is well developed. However, the chemistry of these metals in the +1 oxidation state with these ligands has not received much attention. Thus, in order to obtain palladium(I) complexes, we explored the redox reaction involving palladium(0) and palladium(II) complexes. In all these reactions, however, only palladium(II) complexes were found. The crystal structure of the title compound, (I), has been determined and is presented here.



(I)



(*b*)

Fig. 1. The structure of (*a*) molecule *A* and (*b*) molecule *B*, showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.