Metal-Phenoxyalkanoic Acid Interactions. Part 11*. Crystal Structure of Potassium 2,4-Dichlorophenoxyacetate Hemihydrate

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Introduction

Previous work by this group on the interaction of the phenoxyalkanoic acid herbicides with metal ions and the elucidation of the nature of the complexes formed has been primarily involved with the divalent metal series Mg, Mn, Co, Ni, Cu, Zn ([1] and references therein). An extension of this work has now been made into the area of the Groups IA and IIA metals since these are now recognized as being important in biological interactions and all transfer processes. A series of these complexes has now been prepared and the X-ray structure of the potassium salt of 2,4-dichlorophenoxyacetic acid (2,4-D) is reported here.

Experimental

Preparation

The title compound was prepared by titration of an aqueous ethanolic solution of 2,4-dichlorophenoxyacetic acid to the phenolphthalein end point with a 0.1 *M* solution of potassium hydroxide. The solution of the salt was allowed to evaporate at room temperature and the crystals obtained were purified by recrystallization from water.

Crystal Data

$C_8H_6Cl_2KO_{3.5}$, M = 268.1, monoclinic, a = 36.80(1), b = 4.339(1), c = 12.975(7) Å, β = 102.03(4)°, U = 2026 Å^3, D_m = 1.73 gcm^{-3} (by flotation), D_c = 1.76 gcm^{-3}, Z = 8, F(000) = 1080, λ = 0.7107 Å, μ(Mo-Kα) = 10.2 cm^{-1}, space group C2/c (C_{2h}^6, No. 15).

X-Ray Data Collection, Structure Solution and Refinement

Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. The intensities of 2853 reflections were measured up to 2θ = 50° from a single crystal (0.30 × 0.20 × 0.06 mm) (1537 unique) of which 1344 with $I > 2.5\sigma(I)$ were considered observed and were used in structure analysis.

The structure was solved by direct methods using SHELX [2] and refined by full-matrix least squares to a final $R\{=\Sigma||F_o| - |F_c||/\Sigma F_o\} = 0.034$ and an R_w-$[=(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}] = 0.034$ with $w = 1.1/\sigma^2 F_o - 0.002\ F_o)$. Data were not corrected for absorption or extinction while neutral atom scattering factors were used [3, 4], the K being corrected for anomalous dispersion [5]. Hydrogen atoms were located in a difference-Fourier synthesis and their positional and thermal parameters were allowed to refine.

TABLE I. Atomic Coordinates (×10^4, except H, ×10^3).

	x/a	y/b	z/c
K	321.0(2)	2534(2)	1278.6(5)
C(1)	1376.6(8)	2304(8)	547(2)
C(2)	1484.0(8)	4055(8)	1461(2)
Cl(2)	1176.5(2)	4475(3)	2297.1(6)
C(3)	1825.8(9)	5431(9)	1716(2)
C(4)	2070.8(8)	5096(8)	1061(2)
Cl(4)	2509.2(2)	6739(3)	1394.7(7)
C(5)	1971.6(9)	3422(9)	151(2)
C(6)	1628.0(9)	2056(8)	−106(3)
O(7)	1033.9(5)	993(6)	367(1)
C(8)	936.1(9)	−792(9)	−582(2)
C(9)	575.1(8)	−2537(7)	−654(2)
O(10)	397.9(6)	−2327(5)	55(2)
O(11)	487.8(6)	−4067(6)	−1486(2)
Ow	0	−1659(10)	2500
H(3)	188.6(9)	668(9)	230(3)
H(5)	212.1(8)	320(7)	−26(2)
H(6)	156.8(9)	82(9)	−76(3)
H(81)	113.5(9)	−231(8)	−62(2)
H(82)	91.0(9)	49(8)	−122(2)
H(1)	−14(1)	−275(10)	211(3)

Final atomic parameters are listed in Table I while lists of anisotropic thermal parameters together with observed and calculated structure factors are available from the authors. Bond distances and angles are given in Table II. A labelling scheme is shown in Fig. 1.

Discussion

The crystal structure of potassium 2,4-dichlorophenoxyacetate hemihydrate shows potassium ions

*Part 10 ref. [1].

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TABLE II. Bond Distances (Å) and Angles (degrees). Primed Atoms are Symmetry Generated.

a. Distances

K–O(7)	3.167(1)	C(1)–C(2)	1.395(4)
K–O(10)	2.690(2)	C(1)–C(6)	1.383(4)
K–O(10)′	2.786(2)	C(1)–O(7)	1.359(3)
K–O(10)″	2.845(2)	C(2)–Cl(2)	1.733(3)
K–Ow	2.828(3)	C(2)–C(3)	1.369(4)
K–O(11)	3.116(2)	C(3)–C(4)	1.370(4)
K–O(11)′	2.915(2)	C(4)–Cl(4)	1.735(3)
K–O_w′	3.322(3)	C(4)–C(5)	1.369(5)
		C(5)–C(6)	1.374(5)
K–Cl	3.262(1)	O(7)–C(8)	1.436(4)
		C(8)–C(9)	1.515(4)
		C(9)–C(10)	1.237(4)
		C(9)–O(11)	1.251(4)

b. Angles

O(7)–K–O(10)	54.3	C(2)–C(1)–C(6)	117.1(3)
O(7)–K–O(10)′	76.4	C(2)–C(1)–O(7)	117.5(3)
O(7)–K–O(10)″	120.3	C(6)–C(1)–O(7)	125.3(3)
O(7)–K–Ow	123.3	C(1)–C(2)–Cl(2)	118.9(2)
O(7)–K–O(11)	163.4	C(1)–C(2)–C(3)	121.7(3)
O(7)–K–O(11)′	113.6	Cl(2)–C(2)–C(3)	119.4(2)
O(10)–K–O(10)′	104.8	C(2)–C(3)–C(4)	119.7(3)
O(10)–K–O(10)″	79.3	C(3)–C(4)–Cl(4)	120.0(3)
O(10)–K–Ow	86.2	C(3)–C(4)–C(5)	120.0(3)
O(10)–K–O(11)	116.0	Cl(4)–C(4)–C(5)	120.0(2)
O(10)–K–O(11)′	137.8	C(4)–C(5)–C(6)	120.3(3)
O(10)′–K–O(10)″	82.6	C(1)–C(6)–C(5)	121.2(3)
O(10)′–K–Ow	159.8	C(1)–O(7)–C(8)	115.5(2)
O(10)′–K–O(11)	95.2	O(7)–C(8)–C(9)	112.5(2)
O(10)′–K–O(11)′	111.1	C(8)–C(9)–O(10)	120.6(3)
O(10)′–K–O(11)	82.9	C(8)–C(9)–O(11)	112.5(3)
O(10)″–K–O(11)	86.3	O(11)–C(9)–O(10)	126.9(3)
O(10)″–K–O(11)	43.5		
O(10)″–K–O(11)′	126.1		
Ow–K–Ow′	89.3		
Ow–K–O(11)	64.6		
Ow–K–O(11)′	67.3		
O(11)–K–O(11)′	82.7		

Final parameters and esds for Potassium 2,4-Dichlorophenoxyacetic acid. $5H_2O$.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
K	369(4)	332(6)	374(4)	4(3)	78(3)	−17(3)
C(1)	287(15)	281(25)	287(15)	39(13)	17(11)	−15(13)
C(2)	342(16)	358(24)	273(14)	17(14)	70(11)	11(14)
Cl(2)	456(5)	770(9)	357(4)	−154(4)	163(3)	−125(4)
C(3)	408(18)	383(26)	294(16)	−23(16)	10(13)	−58(15)
C(4)	311(16)	350(25)	377(17)	42(14)	33(13)	−53(14)
Cl(4)	383(5)	640(8)	506(5)	−47(5)	59(4)	−191(4)
C(5)	371(17)	413(27)	373(17)	−4(16)	152(14)	−12(15)
C(6)	371(16)	367(26)	319(16)	−44(15)	64(13)	−27(15)
O(7)	307(11)	423(16)	305(10)	−77(10)	78(8)	−66(10)
C(8)	346(16)	299(24)	282(15)	−54(15)	58(12)	−7(15)
O(10)	368(11)	405(18)	407(12)	9(11)	115(10)	−40(10)
O(1)	530(29)	360(34)	516(28)	–	−18(22)	–
C(9)	339(15)	215(24)	315(16)	59(14)	18(13)	51(13)
O(11)	451(13)	416(18)	412(13)	−91(12)	20(10)	−105(12)

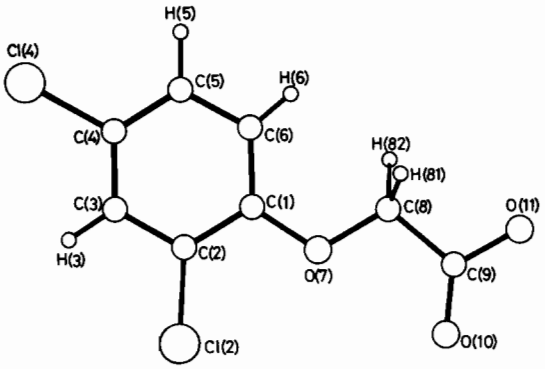

Fig. 1. Labelling scheme and conformation of the 2,4-Dichlorophenoxyacetic Acid Group.

surrounded by an irregular sphere of 8 oxygens; two from water molecules [K–O_w, 2.828(3), 3.322(3) Å], five from the carboxyl oxygens of the 2,4-D anions [K–O, 2.690–3.116(2) Å], one from the phenoxy oxygen at 3.167(1) Å; and one chlorine [K–Cl, 3.262(1) Å]. The long K–phenoxy oxygen link is consistent with general metal–phenoxy oxygen interactions except in some Cu(II) complexes where coordination and carboxyl oxygen are observed. In such examples as $[Cu(Ar–O–CH_2COO)_2(H_2O)_2$ (Ar = phenyl [6]; Ar = 4-chlorophenyl [7]; Ar = 4-methoxyphenyl [8], the axial elongation about the coordination sphere allows the accommodation of the longer O(ether)···O(carboxyl) span which is a relatively constant dimension in both free and complexed acids [7]. In this example, the distance [O(7)···O(10)] is 2.706(4) Å and compares with 2.717(6) Å in 2,4-dichlorophenoxyacetic acid [9].

Although bond distances and angles in the 2,4-D anion are similar to those of the free acid, where the acetic acid residue is synclinally related to the ring system, in this salt, the two are essentially coplanar. The reverse is the case for sodium phenoxyacetate hemihydrate [10] (synclinal) compared with phenoxyacetic acid [11] which is planar.

Torsion angles within the side chain [C(2)–C(1)–O(7)–C(8), C(1)–O(7)–C(8)–C(9), O(7)–C(8)–C(9)–O(10)] are 180°, +172°, 0°; −179°, 80°, 0°, for this example and 2,4-D respectively. Retention of the synplanar-synplanar side chain conformation of the free acid is also observed, based on the criteria of exo-carboxyl angles [7] [C(8)–C(9)–O(10) (carboxyl) and C(8)–C(9)–O(11) (hydroxyl)] which are 120.6(3)° and 112.5(3)° respectively.

The water molecules (Ow) in this structure are located at special positions on the crystallographic two-fold rotation axes (at z = $\frac{1}{4}$, $\frac{3}{4}$) and are shared by the K^+ cations and the $(2,4\text{-}D)^-$ anions which are related by the same two-fold symmetry (Fig. 2). These form alternating chains comprising a. K^+ and oxygens (waters, carboxyls) and b. 2,4-dichlorophenyl rings.

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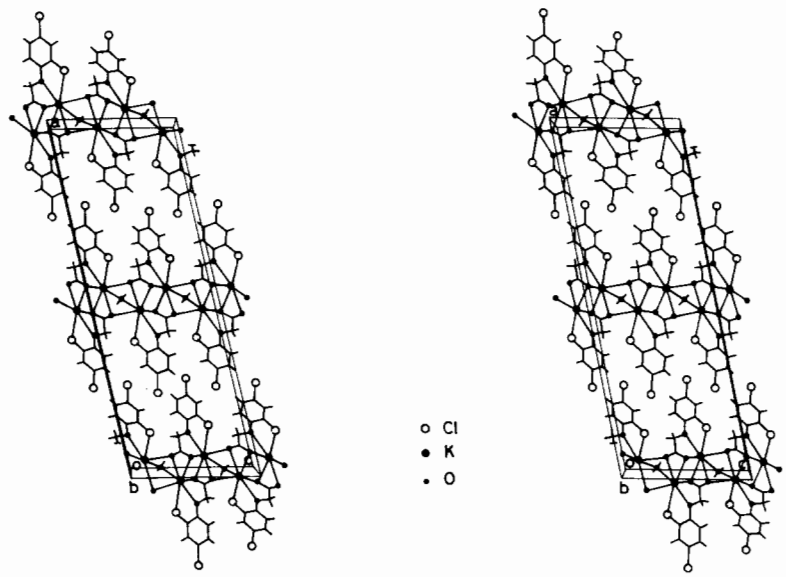

Fig. 2. Stereoview of the packing in the unit cell viewed down the b axis.

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