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Metal–Phenoxyalkanoic Acid Interactions.
Part 4. The Crystal Structure of Tetraaquabis(2,4,5-trichlorophenoxyacetato)-manganese(II)-Bis(2,4,5-trichlorophenoxyacetic acid) Adduct

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The crystal structure of tetraaquabis(2,4,5-trichlorophenoxyacetato)manganese(II)-bis(2,4,5-trichlorophenoxyacetic acid) adduct has been determined by X-ray diffraction from diffractometer data and refined by least-squares to R *0.054 using 2142 'observed' reflections. The crystals are triclinic, space group* $P\bar{1}$ *with Z = 1 in a cell of dimensions* $a = 7.456(5)$, $b = 20.841(12)$, $c = 7.175(4)$ Å, $\alpha = 90.70(4)$, $\beta = 99.18(5)$, $\gamma = 77.11(5)°$. *The complex consists of slightly distorted centrosymmetric octahedral* MnO_6 *units involving four aqua ligands [Mn–O, 2.190(5), 2.232(5) Å] and two oxygens from unidentate* trans-*related 2,4,5-trichlorophenoxyacetate ligands [Mn–O, 2.146(5) Å]. The uncoordinated carboxyl oxygens are bound* via *very short hydrogen bonds [O······O, 2.459(8) Å] to two adducted 2,4,5-trichlorophenoxyacetic acid molecules which layer in the structure with their benzene rings approximately parallel to those of the coordinated acid ligands.*

Introduction

As part of a continuing study of complexes formed by the interaction of metal ions with the phenoxyalkanoic acid herbicides, a number of crystal structures have been determined using X-ray methods [1–3]. Manganese(II) complexes of the phenoxy acid series are of particular interest since polymers predominate among carboxylate complexes of this species (see ref. 2 and examples therein). The complexes diaquabis(phenoxyacetato)manganese(II) and diaquabis(*p*-chlorophenoxyacetato)manganese(II), which are isostructural and isomorphous with their magnesium(II) and cobalt(II) analogues have six-coordinate octahedral stereochemistries with *trans*-related aqua ligands and carboxylate oxygens bridging metal centres in a two-dimensional polymeric mode [2]. In contrast, the discrete monomeric species are rare, *e.g.* tetraaquabis(4-aminobenzoato)manganese(II) [4] and *cis*-diaquadichlorobis(glycine)manganese(II) [5]. The structure of the title complex was determined to aid in a better understanding of metal–phenoxyalkanoic acid interactions and to compare the conformational aspects of coordinated and uncoordinated 2,4,5-trichlorophenoxyacetic acid (2,4,5-T·H.) [6].

Experimental

Preparation of $Mn(H_2O)_4(2,4,5\text{-}T)_2\cdot 2(2,4,5\text{-}T\cdot H)$ *[where 2,4,5-T·H = 2,4,5-trichlorophenoxyacetic acid; and 2,4,5-T = 2,4,5-trichlorophenoxyacetato ligand]*

A solution of 1.0 g of 2,4,5-trichlorophenoxyacetic acid in a minimum volume of boiling aqueous ethanol was reacted with manganese(II) carbonate. After digestion for *ca.* 1 hour, the excess carbonate was removed by vacuum filtration and washed with ethanol. The filtrate, on standing at room temperature in an open container for several days, gave pink platey crystals which analysed as $[Mn(2,4,5\text{-}T)_2(H_2O)_5]$ [found: C, 29.5; H, 2.81; Cl, 32.2%: calc. for $C_{16}H_{18}Cl_6O_{11}Mn$: C, 29.4; H, 3.07; Cl, 32.5%]. This microcrystalline product was unsuitable for structural work. However crystals from a second crop were suitable. A subsequent structure determination confirmed that the crystal had free 2,4,5-trichlorophenoxyacetic acid. An anomalous crystal

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TABLE I. Experimental Data for the X-Ray Diffraction Study of $[Mn(H_2O)_4(2,4,5\text{-}T)_2 \cdot 2(2,4,5\text{-}T \cdot H)]$, $C_{32}H_{26}Cl_{12}MnO_{16}$.

A. Crystal Parameters[a] *at 25 °C*

Crystal system:	triclinic
Space group:	$P\bar{1}$
a = 7.456(5) Å	α = 90.70(4)°
b = 20.841(12) Å	β = 99.18(5)°
c = 7.175(4) Å	γ = 77.11(5)°
V = 1072.6 Å^3	
Z = 1	
Mol. wt. = 1146.6	
ρ(calcd) = 1.78 g cm^{-3}	
ρ(found) = 1.80 g cm^{-3}	
F(000) = 575	

B. Measurement of Data

Diffractometer:	Syntex $P2_1$
Radiation:	Mo $K\alpha$ (λ = 0.7107 Å)
Monochromator:	graphite, equatorial mode
Reflexions measured:	h = +7; k = (±)21; l = (±)8
2θ range:	5–50°
Scanning mode:	$2\theta/\theta$
Reflexions collected:	3702 total; 3214 unique
Standards:	3 0 0; 0 0 2; 0 5 –1
Abs. coeffic.	μ(Mo $K\alpha$) = 11.36 cm^{-1} no corrections applied.
Crystal size	0.15 × 0.04 × 0.30 mm

[a] Accurate cell parameters were obtained by least-squares refinement of angle data for twelve reflexions using the Syntex system.

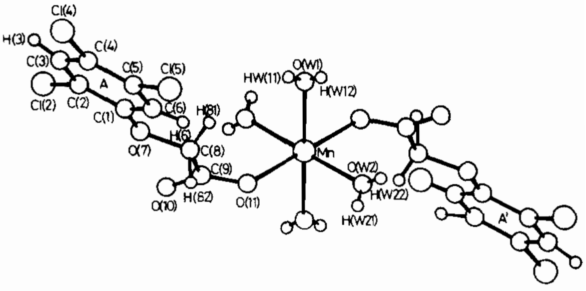

Fig. 1. Molecular configuration and atom naming scheme for $[Mn(H_2O)_4(2,4,5\text{-}T)_2 \cdot 2(2,4,5\text{-}T \cdot H)]$.

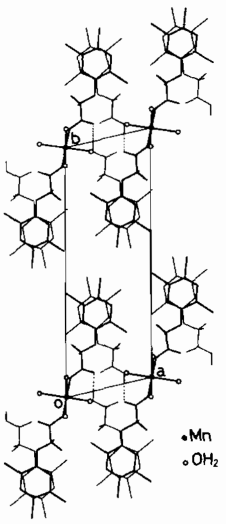

Fig. 2. Packing perpendicular to the *ab* plane.

density (1.80 g cm^{-3}), was inconsistent with the initially proposed 5-hydrate. The structure solution thus confirmed the existence of two distinctly different crystalline complexes, the adducted form of the present analysis and another, probably a more conventional complex.

Collection of X-Ray Data and Structure Solution

A flat crystal plate (0.15 × 0.04 × 0.30 mm) aligned about the c (prism) axis was used for preliminary X-ray examination and data collection. Three-dimensional X-ray diffraction data were obtained from the crystal mounted on a

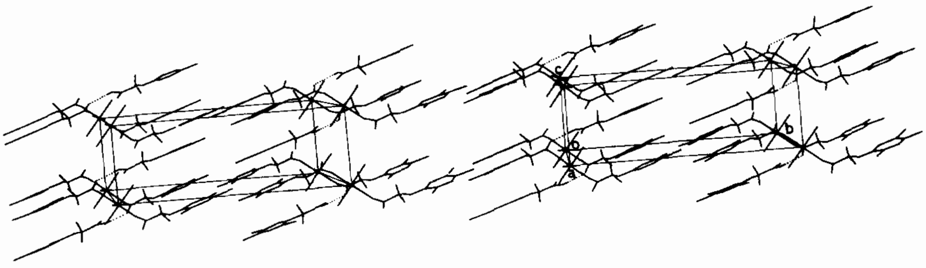

Fig. 3. Stereoscopic view of packing in the cell perpendicular to the *bc* plane.

TABLE II. Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses. A and B represent the coordinated and un-coordinated 2,4,5-T molecules respectively. Naming convention follows that for 2,4,5-trichlorophenoxyacetic acid (2,4,5-T•H) [6].

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Mn	0	0	0	H(W11)	571	783	2459
O(W1)	98(8)	669(3)	2450(10)	H(W12)	1058	650	2972
O(W2)	–3011(8)	394(3)	–700(10)	H(W21)	–3470	644	–1573
				H(W22)	not located		
	Molecule A				Molecule B		
C(1)	3468(10)	2476(3)	–362(11)		3556(11)	2500(4)	–5263(11)
C(2)	5191(10)	2635(4)	90(11)		1730(11)	2882(4)	–5342(11)
C(3)	5392(13)	3247(4)	743(11)		1396(14)	3530(4)	–4825(12)
C(4)	3795(12)	3721(4)	926(11)		2878(12)	3826(4)	–4204(11)
C(5)	2079(11)	3569(3)	461(11)		4667(11)	3454(4)	–4111(10)
C(6)	1885(12)	2951(3)	–154(11)		5016(13)	2796(4)	–4639(11)
O(7)	3458(7)	1854(2)	–973(8)		3706(7)	1875(2)	–5880(8)
C(8)	1708(12)	1672(4)	–1156(15)		5530(12)	1470(4)	–5609(14)
C(9)	1851(14)	981(4)	–1905(13)		5385(13)	790(4)	–6363(11)
O(10)	3238(8)	717(3)	–2637(9)		3952(8)	674(3)	–7205(9)
O(11)	472(8)	747(3)	–1774(9)		6977(8)	368(3)	–6043(8)
Cl(2)	7179(3)	2036(1)	–140(3)		–121(3)	2515(1)	–6126(4)
Cl(4)	4032(3)	4495(1)	1655(3)		2419(3)	4633(1)	–3564(3)
Cl(5)	38(3)	4157(1)	587(4)		6550(3)	3797(1)	–3347(4)
H(3)	6692	3258	1270		137	3789	–4627
H(6)	601	2865	–348		6391	2532	–4439
H(81)	1536	1610	10		6087	1472	–4070
H(82)	567	2080	–2559		6411	1642	–6700
H(11)		–			6982	–159	–6521

TABLE III. Anisotropic Thermal Parameters (Å^2. $\times 10^3$) for $[Mn(2,4,5\text{-}T)_2(H_2O)_4 \cdot 2(2,4,5\text{-}T \cdot H)]$.[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn	40(1)	32(1)	97(2)	–15(1)	1(1)	–18(1)						
O(W1)	51(4)	51(3)	99(5)	–23(3)	3(4)	–22(3)						
O(W2)	46(4)	54(4)	87(5)	–4(4)	–8(3)	–8(3)						
	Molecule A						*Molecule B*					
C(1)	37(4)	26(4)	43(5)	–7(4)	6(4)	–15(4)	38(5)	41(5)	38(5)	–3(4)	3(4)	–16(4)
C(2)	36(5)	32(4)	46(5)	–5(4)	11(4)	–7(4)	44(6)	52(6)	46(6)	–16(4)	5(4)	–26(5)
C(3)	42(6)	39(4)	44(5)	–4(4)	–2(4)	–19(4)	46(7)	51(6)	50(6)	–7(4)	14(5)	–3(5)
C(4)	62(6)	29(4)	33(5)	–6(4)	3(4)	–15(4)	56(6)	35(5)	40(6)	–10(4)	8(4)	–17(4)
C(5)	47(5)	27(4)	43(6)	–2(4)	8(4)	–7(4)	45(5)	41(5)	38(5)	–15(4)	13(4)	–20(4)
C(6)	37(5)	27(4)	44(5)	–3(4)	7(4)	–9(4)	45(6)	39(5)	46(6)	–11(4)	11(5)	–12(4)
O(7)	32(3)	31(3)	72(4)	–18(3)	9(3)	–16(2)	46(4)	33(3)	66(4)	–18(3)	3(3)	–14(3)
C(8)	49(6)	38(5)	53(8)	–7(5)	9(5)	–20(4)	49(6)	32(4)	60(7)	–15(4)	4(5)	–14(4)
C(9)	59(6)	24(4)	63(6)	3(4)	–9(5)	–13(5)	59(7)	44(5)	41(6)	–17(4)	15(5)	–25(5)
O(10)	54(4)	38(4)	83(5)	–20(3)	11(3)	–15(3)	49(4)	54(5)	85(5)	–32(3)	7(3)	–28(3)
O(11)	51(4)	34(3)	117(6)	1(3)	41(4)	–23(3)	50(4)	44(4)	82(4)	–18(3)	–7(3)	–9(3)
Cl(2)	36(1)	51(1)	86(2)	–20(1)	6(1)	–9(1)	77(2)	40(1)	73(2)	–20(1)	14(1)	–9(1)
Cl(4)	93(2)	35(1)	66(2)	–18(1)	9(1)	–32(1)	44(1)	76(2)	87(2)	–27(1)	7(1)	–29(1)
Cl(5)	60(2)	35(1)	82(2)	–16(1)	14(1)	2(1)	57(2)	54(1)	81(1)	–23(1)	16(1)	–32(1)

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

TABLE IV. Interatomic Distances (A) and Angles (degrees) for [Mn(2,4,5-T)$_2$(H$_2$O)$_4$·(2,4,5-T·H)$_2$]. Intra-ligand and intra-adduct values are compared with those for 2,4,5-T acid [6].

a. Coordination sphere

(i) Distances		*(ii) Angles*	
Mn–O(W1)	2.232(5)	O(W1)–Mn–O(W2)	89.52(2)
Mn–O(W2)	2.190(5)	O(W1)–Mn–O(11A)	89.97(2)
Mn–O(11A)	2.146(5)	O(W2)–Mn–O(11A)′	90.03(2)
		O(W2)–Mn–O(11A)	89.91(2)

b. Intra-ligand and intra-adduct

(i) Distances

	Molecule A	*Molecule B*	*2,4,5-T·H*[6]
C(1)–C(2)	1.386(9)	1.408(9)	1.391(9)
C(2)–C(3)	1.385(9)	1.375(10)	1.383(9)
C(2)–Cl(2)	1.740(6)	1.738(7)	1.726(6)
C(3)–C(4)	1.390(10)	1.393(10)	1.392(8)
C(4)–C(5)	1.375(9)	1.377(9)	1.375(9)
C(4)–Cl(4)	1.726(6)	1.712(7)	1.731(6)
C(5)–C(6)	1.387(8)	1.397(9)	1.401(8)
C(5)–Cl(5)	1.742(7)	1.726(7)	1.734(5)
C(6)–C(1)	1.388(9)	1.380(9)	1.398(8)
C(1)–O(7)	1.363(7)	1.357(7)	1.369(7)
O(7)–C(8)	1.424(8)	1.417(8)	1.417(8)
C(8)–C(9)	1.518(10)	1.531(9)	1.517(7)
C(9)–O(10)	1.249(9)	1.213(8)	1.213(7)
C(9)–O(11)	1.249(9)	1.299(8)	1.301(8)

(ii) Angles

	Molecule A	*Molecule B*	*2,4,5-T·H*[6]
C(1)–C(2)–C(3)	122.6(6)	121.7(7)	121.1(3)
C(1)–C(2)–Cl(2)	118.5(5)	118.2(5)	119.9(3)
C(3)–C(2)–Cl(2)	118.9(6)	120.1(6)	119.1(3)
C(2)–C(3)–C(4)	118.5(7)	120.2(8)	119.5(4)
C(3)–C(4)–C(5)	119.2(6)	118.5(6)	119.5(4)
C(3)–C(4)–Cl(4)	118.6(6)	119.2(6)	119.0(3)
C(5)–C(4)–Cl(4)	122.1(6)	122.3(5)	121.6(3)
C(4)–C(5)–C(6)	122.2(6)	121.6(6)	121.9(3)
C(4)–C(5)–Cl(5)	120.8(5)	120.2(5)	121.4(3)
C(6)–C(5)–Cl(5)	117.0(6)	118.2(6)	116.6(3)
C(5)–C(6)–C(1)	119.1(7)	120.3(7)	118.1(4)
C(6)–C(1)–C(2)	118.5(6)	117.8(7)	119.8(3)
C(6)–C(1)–O(7)	124.6(6)	126.0(7)	124.0(4)
C(2)–C(1)–O(7)	117.0(6)	116.1(6)	116.1(3)
C(1)–O(7)–C(8)	115.7(6)	115.9(5)	117.0(3)
O(7)–C(8)–C(9)	111.0(6)	107.5(6)	106.7(3)
C(8)–C(9)–O(10)	119.1(7)	123.1(7)	122.9(4)
C(8)–C(9)–O(11)	114.0(8)	112.0(6)	112.7(3)
O(10)–C(9)–O(11)	126.8(7)	124.9(7)	124.4(4)

Syntex $P2_1$ four-circle diffractometer, as described in Table I.

Data were corrected for Lorentz polarization and monochromator polarization effects but not for absorption [μ(Mo $K\alpha$) = 11.4 cm^{-1}]. Intensity statistics for the data [mean (E^2 − 1) = 0.953] indicated that the space group was centrosymmetric ($P\bar{1}$). However, the structure could not be solved by the heavy atom method with Mn alone placed at the origin. The automatic centrosymmetric Σ_2

direct methods approach and the tangent refinement methods of SHELX [7] were likewise unsuccessful. However, the structure was solved using MULTAN [8] with 400 Es generating 4457 Σ_2 relationships. 30 of the 31 non-hydrogen atoms were located in an E-map and isotropic refinement (R = 0.21) and a difference-Fourier synthesis revealed the last atom. All but one hydrogen were located in a difference-Fourier at R = 0.064 (all non-hydrogens anisotropic) and included in the calculations with their positional parameters being refined but the isotropic U's set invariant at 0.05 Å^2. This yielded a final $R[=\Sigma\|F_o - F_c\|/\Sigma|F_o|]$ of 0.054 and $Rw[=\Sigma w(\|F_o - F_c\|^2/\Sigma w|F_o|^2)^{1/2}]$ of 0.05 for 2142 reflexions with $I > 3\sigma(I)$. A value of $w = 2.389/(\sigma^2\ F_o)$ was found to be suitable. A final difference-Fourier revealed no features larger than 0.17 eÅ^{-3}. Scattering factors used were: non hydrogens [9] and hydrogen [10]. No corrections were made for extinction. Final atomic positional and thermal parameters are listed in Tables II and III.

Discussion

The coordination sphere about the Mn^{II} ions in the complex (Fig. 1) consists of a slightly distorted centrosymmetric octahedron with four oxygens from water ligands [Mn–O, 2.190(5), 2.232(5) Å] and two from *trans*-related unidentate 2,4,5-trichlorophenoxyacetate ligands [Mn–O, 2.146(5) Å). This is similar to that found in the complex tetraaquabis(phenoxyacetato)nickel(II) [11]. This unit is hydrogen bonded through the uncoordinated carboxyl oxygens to two free 2,4,5-T acid molecules (O•••O, 2.459(8) Å, O–H–O, 169.1°) to give a 1:2 adduct (Fig. 2). These free acid molecules layer in the structure parallel to the bonded 2,4,5-T ligands down the approximate *c* direction in the cell with an inter-layer separation of *c*/2 (3.59 Å) (Fig. 3). The presence of π–π interactions between these rings probably stabilizes their orientation in the structure. Similar adducted but neutral molecules have been found in metal complex structures, *e.g.* $[Sr(H_2O)_4(phen)_2](ClO_4)_2 \cdot 2phen$ and its Ba analogue [12] [the inter-layer (bonded to adducted) phen distances, 3.534 Å (Sr), 3.516 Å (Ba)], $[Cu(tu)_2(phen)]I \cdot phen$ [13] and $[Ni(OPDA)_4]Cl_2 \cdot 2OPDA$ [14]*. So far in the literature, adducted hydrogen bonded free acids are not common but have been associated with square planar complexes, *e.g.* $2[Pt(gly)_2](H_2C_2O_4 \cdot 2H_2O)$ [15] with O•••O (gly-ox) of 2.70, 2.77 Å. In the present example the shortness of the O•••O bond is typical for acid salts of carboxylic acids [16, 17] and may be considered analogous to these examples in that this system is half the normal hydrogen bonded cyclic dimer unit found in 19 examples of phenoxyalkanoic acids [18] (mean O•••O, 2.645 Å). Although the coordinates of the acid proton have not been refined, its position does not indicate a symmetric hydrogen bond which is common with acid salts. The formation of the adducted structure may be the result of dissociation of a comparatively weaker Mn–O (carboxyl) bond with subsequent reformation of the stronger hydrogen bond.

Intra-ligand distances and angles in both 2,4,5-T molecules [A(coordinated) and B(adducted)] are very similar and similar to those for the free acid [6] (Table IV). This includes distortion of the exo-C(1) angle and retention of the discrete C–C–O angular features of the carboxylic acid group, even with loss of the acid proton. The planar conformation of the free acid is only slightly changed in both adducted, 2,4,5-T•H and coordinated 2,4,5-T, the dihedral angles between the planes of the benzene ring and the carboxyl group being 4.15, 13.25 and 24.00° respectively. The ring A to ring B dihedral angle is 3.94°.

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*OPDA = *o*-phenylenediamine.

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