

Metal–Phenoxyalkanoic Acid Interactions. Part 9*.**The X-Ray Crystal and Molecular Structure of Bis[μ -2,4,5-trichlorophenoxyacetato-*O*]-bis-[*trans*-diaqua(2,4,5-trichlorophenoxyacetato)manganese(II)].****The Third Chemical Polymorph in the Series of Manganese-2,4,5-T Coordination Complexes**

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The third chemical polymorph of the manganese(II)–[2,4,5-trichlorophenoxyacetic acid] series, a complex with formula $[\text{Mn}_2(2,4,5\text{-T})_4(\text{H}_2\text{O})_4]$, has been prepared and its crystal structure determined by X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ with two dimeric molecules in a cell of dimensions $a = 21.471(4)$, $b = 7.770(3)$, $c = 13.064(4)$ Å, $\beta = 90.41(2)^\circ$. The dimers are centrosymmetric with bis-oxo bridges [Mn–O, 2.35, 2.45(2) Å] from carboxylate oxygens of 2,4,5-T molecules. The distorted pyramidal MO_5 stereochemistry about each Mn is completed by two *trans*-related waters [Mn–O, 2.28, 2.31(2) Å] and an oxygen of a second unidentate 2,4,5-T ligand [Mn–O, 2.46(2) Å]. Symmetrically disposed about the sixth coordination position are two long contacts to the ether oxygen and a ring-substituted chlorine of the bridging 2,4,5-T molecule [Mn–O, 2.96(2) Å; Mn–Cl, 3.07(2) Å]. The manganese sites are only partially occupied (42%) indicating considerable Mn lability in a very stable lattice consisting of water and 2,4,5-T molecules.

Introduction

The reaction of the auxin herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aqueous

ethanol with manganese(II) carbonate results in two different chemical polymorphs. The product which crystallizes early from solution has the formula $[\text{Mn}(2,4,5\text{-T})(\text{H}_2\text{O})_5]^+ [2,4,5\text{-T}]^-$, (1), containing both coordinated and ionic 2,4,5-T molecules [2]. This form is isostructural and isomorphous with its Mg(II) analogue [2]. The second polymorph, formed late in the crystallization in the presence of excess 2,4,5-T acid has the form $\{[\text{Mn}(2,4,5\text{-T})_2(\text{H}_2\text{O})_4] \cdot 2(2,4,5\text{-T} \cdot \text{H})\}$, (2), and consists of monomeric six-coordinate Mn complex units with *trans*-related unidentate 2,4,5-T ligands in addition to adducted 2,4,5-T acid molecules [3].

A third polymorph (3), formed as colourless crystals from a preparation in 95% ethanol, gave an elemental analysis inconsistent with a manganese complex of simple stoichiometry. Furthermore, the density determination (1.75 g cm^{-3}) indicated a formula with less Mn than required for a dihydrate. The crystal structure was determined, (i) to resolve this anomaly and (ii) to compare the bonding and mode of packing in the solid state with those for the polymorphs (1) and (2).

Experimental*(a) Complex Preparation*

Compound (3) was prepared by reacting a boiling 95% ethanolic solution of 2,4,5-trichlorophenoxyacetic acid with excess manganese(II) carbonate using the method previously described [4]. After several days, colourless crystals suitable for X-ray analysis were obtained from the solution.

*Part 8: Aquabis(4-chloro-2-methylphenoxyacetato)bis(pyridine)copper(II) [1].

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TABLE I. Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mn	714(5)	544(16)	-573(9)	Hw(11)	1119	-3189	-320
Ow(1)	1052(8)	-2249(25)	-798(14)	Hw(12)	652	-2132	-653
Ow(2)	449(9)	3383(28)	-501(16)	Hw(21)	542	4282	-1000
				Hw(22)	^a		
	<i>Molecule A</i>			<i>Molecule B</i>			
C(1)	2698(11)	-1029(36)	-3625(18)	2210(10)	941(32)	1199(16)	
C(2)	2989(11)	-1692(33)	-4523(18)	2456(11)	1716(36)	350(19)	
Cl(2)	2551(3)	-2410(11)	-5545(5)	1980(3)	2378(13)	-630(6)	
C(3)	3640(11)	-1877(35)	-4531(19)	3089(11)	1950(35)	297(19)	
C(4)	3986(14)	-1409(42)	-3678(24)	3467(12)	1433(40)	1046(22)	
Cl(4)	4779(3)	-1597(12)	-3743(6)	4271(3)	1743(12)	927(7)	
C(5)	3708(9)	-721(32)	-2902(17)	3232(13)	680(41)	1957(22)	
Cl(5)	4121(3)	-54(11)	-1797(6)	3710(3)	125(12)	2927(6)	
C(6)	3074(8)	-473(28)	-2864(15)	2581(14)	404(45)	1966(24)	
O(7)	2072(7)	-992(23)	-3707(12)	1585(7)	699(23)	1193(12)	
C(8)	1771(10)	-115(32)	-2891(18)	1311(11)	-53(36)	2041(19)	
C(9)	1085(10)	28(35)	-3147(19)	607(11)	-284(37)	1860(20)	
O(10)	831(8)	-583(24)	-3883(13)	356(7)	106(24)	1101(13)	
O(11)	798(7)	963(23)	-2433(12)	339(8)	-1030(23)	2648(14)	
H(3)	3647	-2266	-5202	^a			
H(6)	2934	-34	-2092	2470	109	2687	
H(81)	1896	-818	-2377	1451	730	2676	
H(82)	1836	1291	-2725	1430	-1307	2307	

^aNot located.

TABLE II. Bond Distances (Å) and Angles (degrees).

<i>a. Distances</i>			
Mn-Ow(1)	2.31(2)	Mn-O(10B)	2.45(2)
Mn-Ow(2)	2.28(2)	Mn-O(10B)'	2.35(2)
Mn-O(11A)	2.46(2)	Mn-O(7B)	2.96(2)
		Mn-Mn	3.53(2)
	<i>Molecule A</i>		<i>Molecule B</i>
C(1)-C(2)	1.43(3)		1.37(3)
C(2)-C(3)	1.41(3)		1.37(3)
C(2)-Cl(2)	1.72(2)		1.71(3)
C(3)-C(4)	1.38(4)		1.33(3)
C(4)-C(5)	1.30(4)		1.42(3)
C(4)-Cl(4)	1.71(3)		1.75(4)
C(5)-C(6)	1.38(3)		1.42(3)
C(5)-Cl(5)	1.77(2)		1.68(3)
C(6)-C(1)	1.35(3)		1.34(3)
C(1)-O(7)	1.35(3)		1.36(3)
O(7)-C(8)	1.42(3)		1.39(3)
C(8)-C(9)	1.51(3)		1.54(3)
C(9)-O(10)	1.20(3)		1.17(3)
C(9)-O(11)	1.34(3)		1.32(3)

(continued on facing page)

TABLE II. (continued)

<i>b. Angles</i>			
O(10B)–Mn–O(11A)	165.1(6)	O(11A)–Mn–Ow(1)	88.5(6)
O(10B)–Mn–O(10B)'	85.4(6)	O(11A)–Mn–Ow(2)	86.2(6)
O(10B)–Mn–Ow(1)	95.0(6)	O(11A)–Mn–O(7B)	135.6(7)
O(10B)–Mn–Ow(2)	91.0(8)	Ow(1)–Mn–O(10B)'	93.8(7)
O(10B)–Mn–O(7B)	59.3(6)	Ow(1)–Mn–Ow(2)	173.6(6)
O(11A)–Mn–O(10B)'	79.9(7)	Ow(1)–Mn–O(7B)	86.6(6)
C(9A)–O(11A)–Mn	130.9(6)	Ow(2)–Mn–O(10B)'	81.0(8)
C(9B)–O(10B)–Mn	127.9(6)	Ow(2)–Mn–O(7B)	94.9(7)
Mn–O(10B)–Mn'	94.6(6)	O(10B)'–Mn–O(7B)	144.5(6)
	<i>Molecule A</i>	<i>Molecule B</i>	
C(2)–C(1)–C(6)	117(2)	121(2)	
C(2)–C(1)–O(7)	113(2)	116(2)	
C(6)–C(1)–O(7)	130(2)	123(2)	
C(1)–C(2)–C(3)	119(2)	119(2)	
C(1)–C(2)–Cl(2)	121(2)	120(2)	
C(3)–C(2)–Cl(2)	120(2)	121(2)	
C(2)–C(3)–C(4)	120(2)	121(2)	
C(3)–C(4)–C(5)	119(3)	121(2)	
C(3)–C(4)–Cl(4)	118(2)	119(2)	
C(5)–C(4)–Cl(4)	123(2)	119(2)	
C(4)–C(5)–C(6)	123(2)	115(2)	
C(4)–C(5)–Cl(5)	122(2)	121(2)	
C(6)–C(5)–Cl(5)	115(2)	123(2)	
C(5)–C(6)–C(1)	121(2)	122(2)	
C(1)–O(7)–C(8)	114(2)	119(2)	
O(7)–C(8)–C(9)	108(2)	110(2)	
C(8)–C(9)–O(10)	126(2)	123(2)	
C(8)–C(9)–O(11)	110(2)	111(2)	
O(10)–C(9)–O(11)	124(2)	125(2)	

TABLE III. Comparative Cell Data for the Three Mn(II) Polymorphs of 2,4,5-T. (1), $[\text{Mn}(2,4,5\text{-T})(\text{H}_2\text{O})_5]^+ [2,4,5\text{-T}]^-$, [2]; (2), $[\text{Mn}(2,4,5\text{-T})_2(\text{H}_2\text{O})_4] \cdot 2(2,4,5\text{-T.H})$, [3]; (3), $[\text{Mn}_2(2,4,5\text{-T})_4(\text{H}_2\text{O})_4]$, (This work).

Formula	(1) $\text{C}_{16}\text{H}_{18}\text{Cl}_6\text{MnO}_{11}$	(2) $\text{C}_{32}\text{H}_{26}\text{Cl}_{12}\text{MnO}_{16}$	(3) $\text{C}_{16}\text{H}_{12}\text{Cl}_6\text{Mn}_{0.42}\text{O}_8$
<i>a</i> (Å)	23.122(8)	7.456(5)	21.471(4)
<i>b</i> (Å)	7.560(2)	20.841(12)	7.770(3)
<i>c</i> (Å)	7.066(2)	7.175(4)	13.064(2)
α (°)	90.72(2)	90.70(4)	90
β (°)	86.37(2)	99.18(5)	90.41(2)
γ (°)	88.98(2)	77.11(5)	90
<i>V</i> (Å ³)	1232	1147	2179
<i>D_c</i> (g cm ⁻³)	1.76	1.78	1.73
<i>Z</i>	2	1	4
Space Group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$

(b) Crystal Data

$C_{16}H_{12}Cl_6Mn_{0.42}O_8$, $M = 568.1$, monoclinic, space group $P2_1/c$, $a = 21.471(4)$, $b = 7.770(3)$, $c = 13.064(4)$, $\beta = 90.41(2)^\circ$, $V = 2179 \text{ \AA}^3$, $Z = 4$, $D_c = 1.73 \text{ g cm}^{-3}$, $D_m = 1.75 \text{ g cm}^{-3}$, $F(000) = 1138$, $\mu(\text{Mo-K}\alpha) = 10.7 \text{ cm}^{-1}$.

(c) Collection of X-Ray Data and Structure Solution

3984 reflections (2088 unique) were collected from a single crystal ($0.28 \times 0.12 \times 0.08 \text{ mm}$) mounted about the prism axis on an Enraf-Nonius CAD 4 automatic diffractometer ($2\theta_{\text{max}} = 50^\circ$; graphite monochromated Mo-K α radiation, $\lambda = 0.7107 \text{ \AA}$). Of these, 928 with $I > 2.0\sigma(I)$ were considered observed and were used in structure refinement. The data were not corrected for absorption. The structure was solved using the multi-solution Σ_2 sign expansion direct methods procedure of SHELX [5] which provided all atoms of the 2,4,5-T ligands and the coordinated waters. The manganese, which was later found to have only half occupancy, was subsequently identified among the lower peaks in the initial E-map. Inclusion of the manganese with full occupancy gave poor refinement ($R = 0.14$) compared with the value of $R = [\sum \|F_o - F_c\| / \sum |F_o|] = 0.098$ and $R_w = [\sum w(|F_o - F_c|^2) / \sum |F_o|^2]^{1/2} = 0.094$. A value of $w = 1.62 / [\sigma^2(F_o) + 6.24 \times 10^{-4} (F_o)^2]$ was used. A refined site occupancy factor of 0.42 was obtained for Mn with the isotropic U fixed at 0.040 \AA^2 . Subsequently, refinement involved fixed occupancy and anisotropic thermal parameters for only manganese and chlorines. Most hydrogens were located in difference-Fourier syntheses and included in the refinement at fixed positions with their isotropic thermal parameters set invariant at 0.05 \AA^2 .

The maximum peak in the final difference-Fourier was 0.22 e\AA^{-3} . Scattering factors used were those of Cromer and Mann (non-hydrogens) [6] and Stewart *et al.* (hydrogens) [7]. Final positional parameters are listed in Table I while bond distances and angles are given in Table II. Comparative cell data for the three Mn-2,4,5-T polymorphs are given in Table III.

Discussion

The title complex (**3**) consists of centrosymmetric bis-oxo bridged $[\text{Mn}_2(2,4,5\text{-T})_4(\text{H}_2\text{O})_4]$ dimer units. The MO_5 coordination sphere about each manganese(II) centre has a slightly distorted square pyramidal stereochemistry (Fig 1). The bridging oxygen [O(10B)] is from a carboxylate group of one of the 2,4,5-T ligands (ligand B), and occupies one coordination position in the square plane for one Mn [Mn-O, $2.35(2) \text{ \AA}$] and the apical position for the second Mn [Mn-O, $2.45(2) \text{ \AA}$]. The square plane is com-

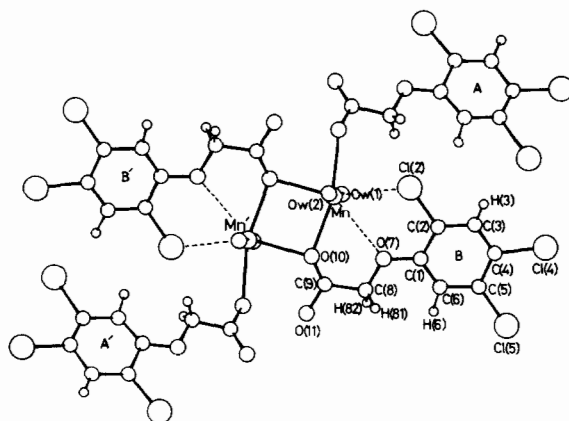


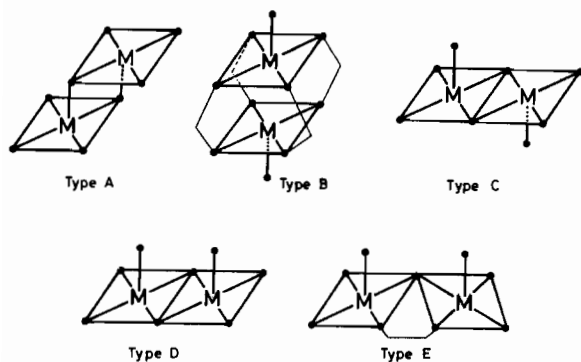
Fig. 1. Molecular configuration and atom numbering scheme for $[\text{Mn}_2(2,4,5\text{-T})_4(\text{H}_2\text{O})_4]$, (**3**). Primed atoms are generated from the named coordinates by the symmetry operation $(-x, -y, -z)$.

pleted by two *trans*-related water ligands [Mn-O, $2.28, 2.31(2) \text{ \AA}$] and the carboxylate oxygen of a second (unidentate) 2,4,5-T ligand [Mn-O, $2.46(2) \text{ \AA}$]. The Mn-Mn separation is $3.53(2) \text{ \AA}$.

Although this bifurcated mode of bridging is known among Mn(II) carboxylates, (**3**) provides a unique example of discrete dimer formation. Manganese acetate tetrahydrate has bis-carboxyl(O,O') bridges as well as a carboxyl(O) bridge giving infinite polymeric chains [8]; manganese propionate dihydrate is also a polymer but has, in addition to carboxyl (O,O') and carboxyl(O) bridges, an aqua(O) bridge [9]; the isostructural and isomorphous manganese phenoxyacetate dihydrate and manganese *p*-chlorophenoxyacetate dihydrate [10] form infinite sheet polymers through carboxyl (O,O') bridges only.

However, other dimeric metal(II) complexes with square pyramidal stereochemistry about each of the metal centres are known and may be classified into a number of different categories. Type A, of which the title compound is a member, has the two square planes parallel with one atom from each plane centred over the metal in the axial position. This type is reviewed by Hodgson [11] and is described by Calderazzo *et al.* [12] as the centrosymmetric axial and basal-edged square pyramids in the classification of binuclear bis-oxo bridged copper(II) compounds. Distortion of the square plane is common and in the case of $[\text{Cu}(t\text{-Bu}(\text{Sal})\text{hfa})_2]$, {bis[1,1,1,5,5,5-hexafluoro-2,4-pentanedionato [N-(2,2-dimethylethyl)-2-hydroxybenzylideneiminato- μ -O] copper(II)]}, the stereochemistry approaches trigonal bipyramidal [13]. Reference [12] also contains a number of examples of Type A complexes.

Other Type A examples not included in [12] are N,N'-ethylenebis(salicylideneiminato)copper(II) [14],



bis(dimethylglyoximato)copper(II) [15], anhydrous copper(II) formate [16] and bis[*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato]cobalt(II) dimer [17].

Type B, exemplified by the dimeric copper(II) acetate structure [18] and other tetracarboxylate metal(II) species, *e.g.* Co(II) and Cr(II) [19, 20] has parallel square planes with each apical group directed away from the other. By far the most common type, it has two examples among the metal phenoxyacetates, tetra- μ -[2,4,5-trichlorophenoxyacetato]-bis[pyridinecopper(II)] [21], and tetra- μ -[2,4-dichlorophenoxyacetato]-bis[aquacopper(II)] dihydrate [21].

Type C, less common than Types A or B has square planes which share a common edge but with the apical groups related by inversion symmetry and is described by Calderazzo [12] as the centrosymmetric basal edged square pyramid. Examples are [di- μ -chloro-*trans*-dichlorobis(2,9-dimethyl-1,10-phenanthroline)dinickel(II)·2-chloroform] [22], bis(1,1,1,7,7,7-hexafluoroheptane-2,4,6-trienato)bis(methanol)dicopper(II) [23], and examples contained in reference [12].

The system with *cis*-related apical groups (Type D), the basal edged square pyramid [12], is a less probable configuration on the basis of stereochemical considerations and has few known examples: [Cu₂(tfacp)₂(OH₂)₂]·H₂O, (tfacp = trifluoroacetyl cyclopentanato) [24] and [Cu₂(pap)₂(OH₂)₂], (pap = N-picolinoyl-3-aminopropoxy), [25]. An example closely resembling Type D is aquatrichlorohydroxo-3,6-bis(2'-pyridyl)pyridazinedicopper(II) [26], classified as Type E. Types D and E appear to be stabilized by the presence of hydrogen bonding between the *cis*-related axial ligands.

In the case of the present example there is a very long contact [2.92(2) Å] in an approximate sixth position in the manganese coordination sphere to the ether oxygen of the B ligand [O(7B)]. In this respect, this example is unique among the Mn(II) phenoxyacetates but resembles examples of the Cu(II) phenoxyacetates, Cu(phenoxy)₂(H₂O)₂ [27], Cu-

(*p*-chlorophenoxy)₂(H₂O)₂ [3], Cu(*p*-methoxyphenoxy)₂(H₂O)₂ [28] and Cu(phenoxy)₂ [29] where the ether oxygens invariably occupy the elongated axial positions of the distorted octahedron [Cu—O: 2.48, 2.41, 2.43, 2.47 Å respectively]. Also symmetrically disposed with respect to manganese and O(7B) is a second long contact to Cl(2B) which appears to be important in the stabilization of the Type A bonding system. The Mn—Cl(2B) distance [3.07(2) Å] must be considered as sufficiently close to be interactive but the chlorine is prevented from approaching closer by the steric interference with the methylene group of ligand A.

The coordination is markedly different from that in (1) or (2) where only unidentate phenoxy ligands are found. Furthermore, there are considerable differences in the Mn—O bond lengths among the three examples. Although the Mn—O_w bonds are longer in (3) than in (1) and (2), these are not considered to be abnormal. The Mn—O(carboxyl) bonds for (3) are abnormally long [2.45, 2.46(2) Å] for manganese carboxylates, indicating that very much weaker bonding exists in this complex. The most stable polymorph (1), in which the MO₆ coordination comprises [Mn(H₂O)₅(2,4,5-T)]⁺ cations, has a short Mn—O(carboxyl) bond [2.07(2) Å]. Insertion of a second 2,4,5-T group into the coordination, giving [Mn(H₂O)₄(2,4,5-T)₂], (2) results in a weakening of this bond, with an increase in the bond length to 2.146(5) Å. The increase to 2.45 Å in (3) is consistent with the considerable lability in the complex and explains the sub-stoichiometric amount of manganese, which was found from site occupancy refinement for this atom. The implication is that the lattice is stable even when only half the Mn sites are occupied. This is feasible considering the nature of the intramolecular interactions which are present in (3) when compared to complexes (1) and (2) as model Mn—(2,4,5-T) systems. In (3) there is not only a very short hydrogen bond [2.46(2) Å] between the coordinated oxygens O(10A) and O(11B) [comparable with 2.46 Å, between a coordinated and an adducted 2,4,5-T acid molecule in (2)] but other intermolecular contacts exist involving O(10A) [to O_w(2), 2.84, 2.97 Å; to O_w(1), 3.06 Å]; and O(11B) [to O_w(1), 2.87 Å]. It was considered that in (1) and (2) [2] the primary factor influencing the formation of these Mn—(2,4,5-T) complexes was the planarity of the 2,4,5-T ring systems. These rings tend to layer in the structures with regular separations [3.53 and 3.59(2) Å in (1) and (2) respectively] indicative of the presence of π — π ring interactions. For (3) the separation is 3.50 Å while the angle between the least-squares planes is 177.8°. The primary difference among all these Mn complexes is that the alternating rings (ligand A and ligand B) have the same relative disposition and superimpose down the *b* axis for (1)

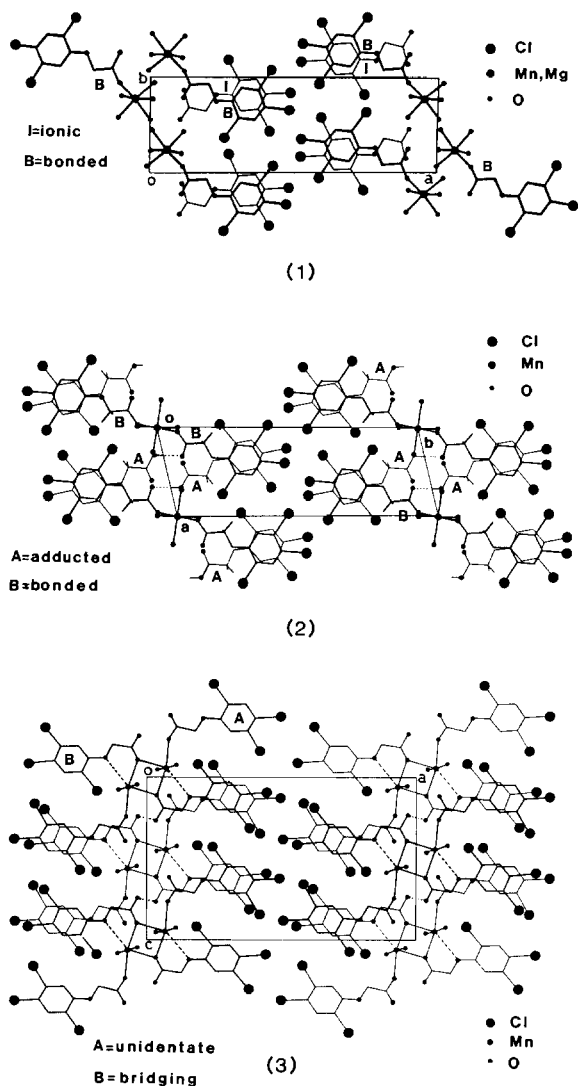


Fig. 2. Comparative packing in their respective cells of the complex polymorphs (1), (2) and (3) (the title compound).

and (2), while in (3) they have a reverse or 'flipped' disposition. A comparison of the three packing modes is made in Fig. 2. From this it is possible to visualise the interconversion of (1) to (2) in the presence of excess 2,4,5-T acid under aqueous conditions. (3) is formed from 95% ethanol with the available water for incorporation in the complex limited so that the interactions involving the (2,4,5-T) ligands become of greater consequence in forming the coordination polyhedron.

Under these conditions, the unidentate ligand (A), which is fixed in the structure by coordination and hydrogen bonding, is analogous to (1) and (2). Ligand (B) must then move into its most sterically favoured coordinating position as well as satisfying the usual six-coordination about Mn. Because of the

positions of the three chlorines in the ring, this involves reversal of the ring orientation of ligand (B) [as found in (1) and (2)], resulting in bridging, along with the secondary stabilization afforded by the longer Mn–O and Mn–Cl contacts. The steric effects of the ring substituents also prevent the formation of the bridging polymeric structure analogous to $[\text{Mn}(\text{phenoxy})_2(\text{H}_2\text{O})_2]_n$ [10].

Within both the 2,4,5-T ligands, the *synplanar-synplanar* conformation of the acid itself [30] is retained. This is also found for all types of 2,4,5-T molecules (bonded, ionic or adducted) in (1) and (2). Torsion angles $[\text{C}(2)\text{--}\text{C}(1)\text{--}\text{O}(7)\text{--}\text{C}(8)$, $\text{C}(1)\text{--}\text{O}(7)\text{--}\text{C}(8)\text{--}\text{C}(9)$ and $\text{O}(7)\text{--}\text{C}(8)\text{--}\text{C}(9)\text{--}\text{O}(11)]$ are $-171^\circ(\text{A})$, $-179^\circ(\text{B})$; $+173^\circ(\text{A})$, $-177^\circ(\text{B})$; $+175^\circ(\text{A})$, $+179^\circ(\text{B})$ respectively compared with the values of $+174$, -172 and $+180^\circ$ for the equivalent angles in 2,4,5-T acid. *Exo*-C(1) angle distortion is likewise retained while the discrete angular difference between the C–C–O bonds of the carboxyl groups allow the origin of the oxygens to be identified as either 'carbonyl' [O(10)] or 'hydroxyl' [O(11)]. Bonding to Mn therefore involves the 'hydroxyl' oxygen of ligand A (unidentate) and the 'carbonyl' oxygen of ligand B (bridging).

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