

Metal-Phenoxyalkanoic Acid Interactions. Part 2.¹ Crystal and Molecular Structures of Diaquabis(phenoxyacetato)manganese(II), Diaquabis(*p*-chlorophenoxyacetato)manganese(II), Diaquabis(phenoxyacetato)cobalt(II), Diaquabis(*p*-chlorophenoxyacetato)cobalt(II), Diaquabis(phenoxyacetato)magnesium(II), and Diaquabis(*p*-chlorophenoxyacetato)magnesium(II)

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The crystal structure of diaquabis(phenoxyacetato)manganese(II) (1) has been determined by X-ray diffraction from diffractometer data and refined by least squares to R 0.047 for 1 189 observed reflections. Crystals are orthorhombic, space group $Pbca$ with $Z = 4$ in a cell of dimensions $a = 7.007(4)$, $b = 7.699(4)$, and $c = 33.219(19)$ Å. The metal atom is at a centre of symmetry with the co-ordination sphere consisting of six oxygens, two from *trans* related waters [2.216(2) Å] and four from carboxylates [2.155(2), 2.148(2) Å] forming a two-dimensional polymer in the ab plane at $z = 0, \frac{1}{2}$. The manganese ions in this plane are 5.21 Å from one another while in the z direction the separation is 16.6 Å. The phenoxyacetato-ligands lie approximately parallel to the z axis and adopt the synplanar (*syn-syn*) conformation characteristic of the unco-ordinated phenoxyacetic acid. Powder diffractometer data, preliminary single-crystal X-ray photographs, and chemical analysis confirm that diaquabis(*p*-chlorophenoxyacetato)manganese(II) (2), diaquabis(phenoxyacetato)cobalt(II) (3), diaquabis(*p*-chlorophenoxyacetato)cobalt(II) (4), diaquabis(phenoxyacetato)magnesium(II) (5), and diaquabis(*p*-chlorophenoxyacetato)magnesium(II) (6) are isomorphous and isostructural with (1).

INTERACTION of phenoxyalkanoic acids with metal carbonates in aqueous ethanol is known to produce complexes of the type $M^{II}(O_2CROPh)_2(OH_2)_m$ where $M = Mn, Co, Ni, Cu, Zn, \text{ or } Mg$; $O_2CROPh =$ phenoxyalkanoato-ligands; $m = 0-4$. In Part 1 of the series¹ the structures of the tetrahedrally co-ordinated $[Zn(O_2CCH_2OPh)_2(OH_2)_2]$ and its isostructural *p*-chlorophenoxy-analogue were reported, along with the tetragonally distorted octahedral complex $[Cu(O_2CCH_2OC_6H_4Cl-p)_2(OH_2)_2]$.

The manganese(II) complexes are of particular interest because, although the presence of water in the co-ordination sphere obviates tetrahedral stereochemistry of the $[MnCl_4]^{2-}$ type, octahedral co-ordination poses a number of possibilities. The bonding could be similar to the copper(II) examples which involve both the ether and carbonyl oxygens of the phenoxy-ligand in a centrosymmetric monomeric mode. Bonding *via* a symmetrical bidentate carboxylate group is known in the octahedral manganese(I) organometallic acetatobis(carbonyl)bis(triphenylphosphine)manganese(I).² Such a system is extremely rare and should not be expected in the example being considered. Discrete monomers are also known but are not common for manganese(II) carboxylates, *e.g.* tetra-aquabis(hydrogenmaleato)manganese(II),³ *cis*-diaquadichlorobis(glycine)manganese(II),⁴ and bis(*p*-aminobenzoato)tetra-aquamanganese(II)⁵ but most examples involve bridged polymeric structures. Examples of these are manganese(II)-formate dihydrate,^{6,7} -acetate tetrahydrate,⁸ -propionate dihydrate,⁹ -citrate decahydrate,^{10,11} and -malate trihydrate.¹²

Chemical analysis indicated the general formula

$[Mn(O_2CROPh)_2(OH_2)_2]$ for both the manganese(II) phenoxyacetate and *p*-chlorophenoxyacetate complexes while preliminary X-ray data showed both to have similar cells, the same space group ($Pbca$), and four molecules per cell. This was interpreted as meaning that the complex units were centrosymmetric with *trans* related waters and possibly a polymeric structure. Similar cell dimensions and the same space group were found for the analogous cobalt(II) and magnesium(II) complexes, diaquabis(phenoxyacetato)-cobalt(II) (3) and -magnesium(II) (5) and diaquabis(*p*-chlorophenoxyacetato)-cobalt(II) (4) and -magnesium(II) (6) suggesting that they too may be isostructural with the Mn^{II} species. The structure of the manganese(II) complex (1) was determined in order that the question of the mode of bonding be resolved and to ascertain if the synplanar (*syn-syn*) conformation for the free acid is retained in the co-ordinated state. This structure could then be used as a model for the *p*-chloro-analogue (2), the cobalt(II) analogues (3) and (4), and the magnesium(II) analogues (5) and (6).

EXPERIMENTAL

Preparation.— $C_{16}H_{18}MnO_8$ (1), $C_{16}H_{16}Cl_2MnO_8$ (2), $C_{16}H_{18}CoO_8$ (3), and $C_{16}H_{16}Cl_2CoO_8$ (4) were prepared using the general method previously described.¹ For (1); Found: C, 47.8; H, 4.60; Mn, 14.1. Calc. for $C_{16}H_{18}MnO_8$: C, 48.9; H, 4.60; Mn, 14.0%. For (2); Found: C, 41.5; H, 3.60; Cl, 15.7; Mn, 11.8. Calc. for $C_{16}H_{16}Cl_2MnO_8$: C, 41.6; H, 3.50; Cl, 15.4; Mn, 11.9%. For (3); Found: C, 48.2; H, 4.75. Calc. for $C_{16}H_{18}CoO_8$: C, 48.35; H, 4.55% (Co not determined). For (4); Found: C, 41.2; H, 3.50; Cl, 15.0. Calc. for $C_{16}H_{16}Cl_2CoO_8$: C, 41.2; H, 3.45; Cl, 15.2% (Co not determined). For (5); Found:

C, 52.4; H, 5.20. Calc. for $C_{16}H_{18}MgO_8$: C, 52.95; H, 5.00% (Mg not determined). For (6); Found: C, 44.05; H, 3.85; Cl, 16.6. Calc. for $C_{16}H_{16}Cl_2MgO_8$: C, 44.5; H, 3.75; Cl, 16.45% (Mg not determined).

A second crystal modification of cobalt(II) *p*-chlorophenoxyacetate (7), more soluble in ethanol than (4), appeared as needle-like plates during the latter stages of crystallization. Elemental analysis gave C, 38.9; H, 3.90; Cl, 14.2%, corresponding to $[Co(O_2CCH_2OC_6H_4Cl-p)_2(OH)_4]$ (Calc. for $C_{16}H_{20}Cl_2CoO_{10}$: C, 38.3; H, 4.00; Cl, 14.1%) (Co not determined).

Crystals suitable for X-ray analysis were grown from aqueous ethanol as colourless [(1), (2), (5), and (6)] and pink [(3) and (4)] diamond-shaped plates. To date, no crystals of (7) suitable for data collection have been obtained.

X-Ray Data.—(a) *Single-crystal diffractometry.* Data for (1) were obtained from a single crystal measuring $0.25 \times 0.25 \times 0.10$ mm mounted about the *b* axis on a Syntex P2₁ four-circle diffractometer. 1189 Reflections with $I > 2.5\sigma(I)$ were considered observed out of 1394 unique reflections collected up to 2θ 50° using monochromatic Mo- K_α radiation. No correction was made for absorption ($\mu = 8.15$ cm⁻¹). The space group and approximate cell parameters of (2), (3), and (4) were determined from Weissenberg photographs, while for (7), the crystal class was found to be monoclinic.

(b) *Powder diffractometry.* X-Ray powder diffraction patterns of all compounds were recorded at 298 K on a Philips PW1140 powder diffractometer using crystal monochromated Co- K_α radiation ($\lambda = 1.7889$ Å). Indexing of reflections and determination of the accurate cell parameters for (2), (3), (4), (5), and (6) were completed as described elsewhere.¹

Crystal Data.—Diaquabis(phenoxyacetato)manganese(II) (1), $C_{16}H_{18}MnO_8$, $M = 393.2$, Orthorhombic, $a = 7.007(4)$, $b = 7.699(4)$, $c = 33.219(19)$ Å, $U = 1792$ Å³, $D_m = 1.48$ (by flotation), $Z = 4$, $D_c = 1.46$ g cm⁻³, $F(000) = 812$, space group $Pbca$ (D_{2h}^{15} , No. 61), Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu = 8.15$ cm⁻¹.

Diaquabis(*p*-chlorophenoxyacetato)manganese(II) (2), $C_{16}H_{16}Cl_2MnO_8$, $M = 461.9$, Orthorhombic, $a = 7.371(7)$, $b = 7.911(8)$, $c = 31.87(3)$ Å, $U = 1859$ Å³, $D_m = 1.68$ (by flotation), $Z = 4$, $D_c = 1.66$ g cm⁻³, space group $Pbca$.

Diaquabis(phenoxyacetato)cobalt(II) (3), $C_{16}H_{18}CoO_8$, $M = 396.9$, Orthorhombic, $a = 6.839(4)$, $b = 7.593(4)$, $c = 33.23(2)$ Å, $U = 1725$ Å³, $D_m = 1.51$ (by flotation), $Z = 4$, $D_c = 1.53$ g cm⁻³, space group $Pbca$.

Diaquabis(*p*-chlorophenoxyacetato)cobalt(II) (4), $C_{16}H_{16}Cl_2CoO_8$, $M = 465.8$, Orthorhombic, $a = 7.114(11)$, $b = 7.772(13)$, $c = 32.45(5)$ Å, $U = 1794$ Å³, $D_m = 1.71$ (by flotation), $Z = 4$, $D_c = 1.73$ g cm⁻³, space group $Pbca$.

Diaquabis(phenoxyacetato)magnesium(II) (5), $C_{16}H_{18}MgO_8$, $M = 362.4$, Orthorhombic, $a = 7.16(3)$, $b = 7.70(3)$, $c = 33.0(1)$ Å, $U = 1818$ Å³, $D_m = 1.34$ (by flotation), $Z = 4$, $D_c = 1.33$ g cm⁻³, space group $Pbca$.

Diaquabis(*p*-chlorophenoxyacetato)magnesium(II) (6), $C_{16}H_{16}Cl_2MgO_8$, $M = 431.3$, Orthorhombic, $a = 7.35(1)$, $b = 7.80(1)$, $c = 32.71(5)$ Å, $U = 1874$ Å³, $D_m = 1.53$ (by flotation), $Z = 4$, $D_c = 1.53$ g cm⁻³, space group $Pbca$.

Structure Solution.—The structure of (1) was solved by the heavy-atom method. Systematically absent reflections ($0kl$, $k = \text{odd}$; $h0l$, $l = \text{odd}$; $hk0$, $h = \text{odd}$) uniquely defined the space group $Pbca$ so that the four complex

units in the cell must be centrosymmetric with the metal ions occupying special positions at $0, 0, 0, \frac{1}{2}, \frac{1}{2}, 0, 0, \frac{1}{2}, \frac{1}{2}$, and $\frac{1}{2}, 0, \frac{1}{2}$. By placing Mn at the origin, the structure was successfully phased using a weighted difference-Fourier synthesis. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, reduced $R (= \sum ||F_o - F_c| | / \sum |F_o|)$ from 0.66 (Mn only) to 0.047 and $R' (= \sum w ||F_o - F_c| |^2 / \sum w F_o^2)^{1/2}$ to 0.069. Reflections were given the weights $w = 1.00 / [\sigma^2(F_o) + 0.0045(F^2)]$. Hydrogens were located in a difference-Fourier synthesis and included in the refinement at fixed positions with the isotropic U set invariant at 0.05 Å². A final difference Fourier revealed only one peak ($0.4334, 0.5517, -0.1185$) equivalent to $0.5 e \text{ \AA}^{-3}$ above a background of $ca. 0.13 e \text{ \AA}^{-3}$. It is not considered, however, to be significant in this structure. Neutral-atom scattering factors were used^{13,14} while Mn was corrected for anomalous dispersion.¹⁵ No extinction corrections were applied.

Structure amplitudes and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22870 (16 pp.).* Atomic parameters are given in Table 1.

TABLE 1

Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, of diaquabis(phenoxyacetato)manganese(II) (1)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mn	5 000	5 000	0
O(H2)	6 207(3)	6 514(3)	507(1)
O(10)	4 755(3)	2 879(3)	420(1)
O(11)	2 773(3)	1 107(3)	100(1)
C(1)	5 071(5)	-29(4)	1 405(2)
C(2)	6 347(6)	611(5)	1 679(1)
C(3)	6 349(8)	-90(5)	2 073(1)
C(4)	5 118(6)	-1 380(7)	2 182(1)
C(5)	3 859(7)	-2 002(6)	1 901(1)
C(6)	3 794(6)	-1 314(5)	1 511(1)
O(7)	5 146(4)	759(4)	1 032(1)
C(8)	3 737(5)	272(4)	747(1)
C(9)	3 780(4)	1 525(3)	395(1)
H(2)	7 380	1 541	1 591
H(3)	7 397	451	2 291
H(4)	5 106	-1 806	2 471
H(5)	2 901	-3 268	2 005
H(6)	2 759	-1 771	1 306
H(81)	4 066	-904	649
H(82)	2 384	330	850
H(OH1)	6 899	6 191	680
H(OH2)	6 772	7 341	403

DISCUSSION

Diaquabis(phenoxyacetato)manganese(II) (1).—The coordination sphere about Mn in (1) is centrosymmetric consisting of two oxygens from water molecules and four oxygens from phenoxyacetate ligands (Figure 1). Unlike the copper(II) analogues of the same formula, where phenoxyacetate ligands co-ordinate in a bidentate mode using carboxylate and ether oxygens, co-ordination of phenoxyacetate ligands in (1) involves carboxylate oxygens only, one from one ligand, the other from a symmetry generated molecule. This forms a bridge between adjacent Mn centres ($0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0$) separated by 5.21 Å giving two-dimensional polymer structures which lie in the *ab* plane at $z = 0$ and $z = \frac{1}{2}$ while along the *c* direction there are alternating layers of phenoxy-

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

groups and metal centres (with co-ordinated waters) (Figure 2). The Mn-Mn separation is considerably longer than that found for the polymeric manganese(II) propionate dihydrate (3.35 Å) which exhibits temper-

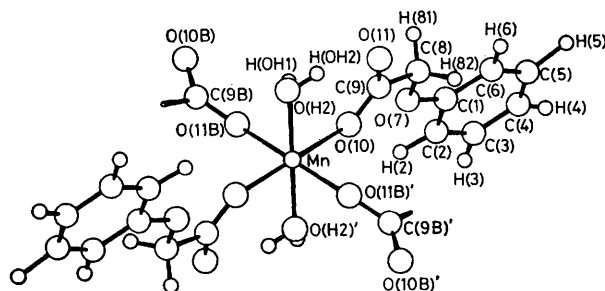


FIGURE 1 Molecular configuration and labelling scheme used for diaquabis(phenoxyacetato)manganese(II) (1). Atoms of the B molecule are generated from the given co-ordinates by the symmetry operations $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$ while the primed atoms are related by inversion through a centre at the metal

ature-dependent magnetic moments (5.9 B.M.) * close to the spin-only value.⁸

Bond distances and angles about the co-ordination sphere are listed in Table 2 indicating a slightly distorted octahedral stereochemistry. The Mn-O(H2) distance [2.216(2) Å] is slightly elongated compared with the Mn-O(carboxylate) distances [2.155(2), 2.148(2) Å] although these distances compare well with the range found for a number of manganese(II) complexes involving co-ordinated water (Table 3). Intraligand distances and angles are shown in Figure 3. These are very similar to the values for the unco-ordinated phenoxyacetic acid¹ which has the same planar *syn-syn* con-

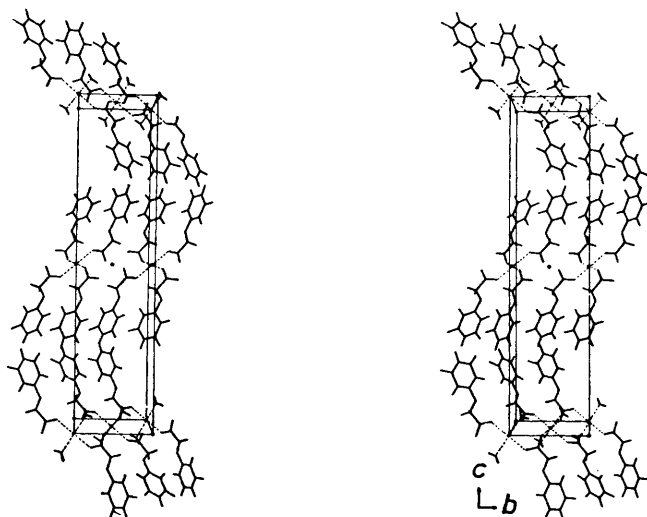


FIGURE 2 Stereoscopic view of the packing of (1) in the cell viewed perpendicular to the *bc* plane

formation. The O(10) (carbonyl) \cdots O(7) (ether) distance in the complex (2.621 Å) compares with 2.671 Å for the free acid. The comparative torsion angles about the C(1)-O(7) and O(7)-C(8) vectors [C(2)-C(1)-O(7)-

C(8) and C(1)-O(7)-C(8)-C(9)] are 174.1, 167.9° and -175.1, 176.1° for the co-ordinated and unco-ordinated acids. The marked inequality of the C-C-O angles about the carboxylic acid group is also used as the means for differentiating between the carbonyl [O(10), 119.4°] and hydroxyl oxygens [O(11), 115.5°] of the carboxyl groups. Both C-O(carbonyl) and C-O(hydroxyl) distances are identical.

Unlike the structures of most manganese(II) complexes of carboxylic acids having water in the co-ordination

TABLE 2

Bond distances (Å) and angles (°) about the co-ordination sphere of $[\text{Mn}(\text{O}_2\text{CCH}_2\text{OPh})_2(\text{OH}_2)_2]$

(a) Distances			
Mn-O(10)	2.155(2)	O(H2)-H(OH1)	0.79
Mn-O(H2)	2.216(2)	O(H2)-H(OH2)	0.83
Mn-O(11B)	2.148(2)		
(b) Angles			
O(10)-Mn-O(H2)	93.62(1)	Mn-O(10)-C(9)	129.29(1)
O(10)-Mn-O(11B)	82.62(1)	Mn-O(11B)-C(9B)	137.25(1)
O(H2)-Mn-O(11B)	91.09(1)		

sphere, the present structure does not derive much stability from hydrogen-bonding interactions. One only intermolecular contact (O \cdots O, 2.816 Å) involving a co-ordinated carboxyl oxygen [O(11)] and a water hydrogen could be found. A longer intraligand contact

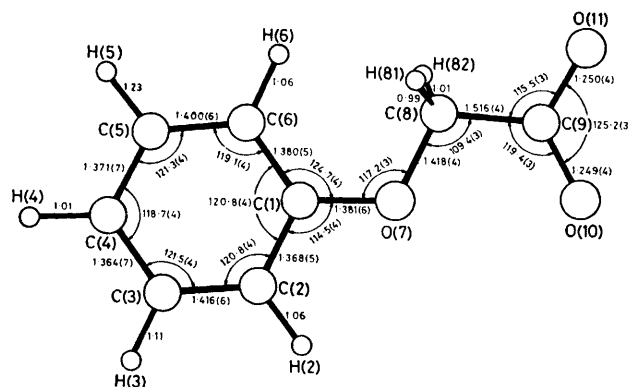


FIGURE 3 Bond distances (Å) and angles (°) about the phenoxyacetato-ligand in (1)

between the carbonyl oxygen and water (2.992 Å) gives the complex unit internal stability.

Diaquabis(p-chlorophenoxyacetato)manganese(II) (2), *Diaquabis(phenoxyacetato)cobalt(II)* (3), *Diaquabis(p-chlorophenoxyacetato)cobalt(II)* (4), *Diaquabis(phenoxyacetato)magnesium(II)* (5), and *Diaquabis(p-chlorophenoxyacetato)magnesium(II)* (6).—Chemical analysis, single-crystal and powder diffractometer X-ray data confirm that compounds (2), (3), (4), (5), and (6) are isostructural with (1). A listing of the indexed powder diffractometer intensities for all compounds is deposited in SUP 22870. Although isostructural manganese(II) and cobalt(II) complexes are not common, the occurrence observed in this group of compounds might be expected considering the similarity in the effective ionic radii [for high-spin, six-co-ordinate Mn^{II} (0.82 Å), Co^{II} (0.74 Å), and Mg^{II} (0.72 Å)].¹⁶ Metal-metal separations

* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m².

within the polymer chain (in the *ab* plane) calculated from the cell parameters are 5.21 (1), 5.41 (2), 5.11 (3), and 5.27 Å (4) giving an increase (Co to Mn) of 0.10 Å [(3) to (1)] and 0.14 Å [(4) to (2)]. This compares with the difference (0.16 Å) calculated from the effective ionic radii. A slight increase in cell volume would also be expected to accommodate the change from Co to Mn, the observed change being 67 and 65 Å³ in going from (3) (1 725 Å³) to (1) (1 792 Å³) and (4) (1 794 Å³) to

analysis showed that loss of two water molecules occurred at low temperature (*ca.* 50 °C) while the remaining two molecules were removed in a one-step process over the temperature range 100–125 °C. Elemental analysis of the powdered sample used for the X-ray powder diffractometry was consistent with a dihydrate, which emphasizes the ease of removal of the lattice water even at room temperature. Verification that the mode of complexation in (7) is similar to

TABLE 3

Manganese(II)–oxygen distances (Å) in metal complexes involving manganese(II) and water molecules in a co-ordination sphere

Complex	Co-ordination sphere	Mn–OH ₂	Mn–O (other)	Ref.
[Mn(O ₂ CCH ₂ OPh) ₂ (OH ₂) ₂] _n	MnO ₄ (OH ₂) ₂	2.22	2.15–2.16	This work
[Mn(OH ₂) ₄][Mn(OH)(Hedta)] ₂ ·4H ₂ O	(i) Mn(OH ₂)(N ₂ O ₃) (ii) MnO ₂ (OH ₂) ₄	2.23 2.15–2.16	2.22–2.26 2.21	<i>a</i>
{[Mn(O ₂ CH) ₂ (OH ₂) ₂] _n }	MnO ₄ (OH ₂) ₂	2.15	2.16–2.21	<i>b</i>
{[Mn(OH ₂) ₆][Mn(O ₂ C ₆ H ₅) ₂ (OH ₂) ₂ ·2H ₂ O] _n }	(i) Mn(OH ₂) ₆ (ii) Mn(O ₂) ₂ (OH ₂) ₂	2.14–2.18 2.14	2.12–2.24 2.15–2.32	<i>c</i> <i>d</i>
{[Mn(O ₂ CMe) ₂ (OH ₂) ₂] _n }	(i) MnO ₄ (ii) MnO ₄ (OH ₂) ₂	2.23–2.27 2.15–2.23	2.16–2.22 2.14–2.19	<i>e</i>
{[Mn(O ₂ C ₆ H ₄)(OH ₂) ₂ ·H ₂ O] _n }	MnO ₄ (OH ₂) ₂	2.22–2.37	2.13–2.21	<i>f</i>
{[Mn(O ₂ CEt) ₂ (OH ₂) ₂] _n }	Mn(OH ₂) ₄ Cl ₂	2.19–2.22		<i>g</i>
[Mn(OH ₂) ₄ Cl ₂]	Mn(OH ₂) ₄ Cl ₂	2.19–2.22		<i>h</i>
{[CsMnCl ₃ ·2H ₂ O] _n }	<i>cis</i> -Mn(OH ₂) ₂ Cl ₄	2.08		<i>i</i>
Cs ₂ MnCl ₄ ·2H ₂ O	<i>trans</i> -Mn(OH ₂) ₂ Cl ₄	2.13		<i>j</i>
Rb ₂ MnCl ₄ ·2H ₂ O	<i>trans</i> -Mn(OH ₂) ₂ Cl ₄	2.08		
α-[RbMnCl ₃ ·2H ₂ O] _n	<i>cis</i> -Mn(OH ₂) ₂ Cl ₄	2.18		<i>k</i>
β-[RbMnCl ₃ ·2H ₂ O] ₂	<i>trans</i> -Mn(OH ₂) ₂ Cl ₄	2.20–2.23		
K[MnCl ₃ ·2H ₂ O]	<i>trans</i> -Mn(OH ₂) ₂ Cl ₄	2.18		<i>l</i>
K ₂ [MnCl ₄ ·2H ₂ O]	<i>trans</i> -Mn(OH ₂) ₂ Cl ₄	2.18		<i>m</i>
Mn[SO ₄ ·K ₂ [SO ₄]]·6H ₂ O	Mn(OH ₂) ₆	2.08–2.17		<i>n</i>
Mn[SO ₄ ·[NH ₄] ₂ [SO ₄]]·6H ₂ O	Mn(OH ₂) ₆	2.15–2.20		<i>o</i>
[Mn(O ₂ C ₆)(OH ₂) ₂]	Mn(O ₂)(OH ₂) ₃	2.11–2.23	2.17–2.25	<i>p</i>
(K ₂ [Mn ^{III} (OH ₂) ₂][Mn ^{III} O(O ₂ CH) ₂]) _n	MnO ₄ (OH ₂) ₂	2.19–2.20	2.19	<i>q</i>
[Mn(OH ₂) ₄ (O ₂ C ₄ H ₇) ₂]	MnO ₂ (OH ₂) ₄	1.98–2.22	2.26	<i>r</i>
[Mn(OH ₂) ₄ (O ₂ C ₆ H ₄ NH ₂ - <i>p</i>) ₂]	MnO ₂ (OH ₂) ₄	2.21–2.22	2.19	<i>s</i>
Mn(NO ₃) ₂ ·H ₂ O	(i) MnO ₄ (OH ₂) ₂ (ii) Mn(O ₂) ₄	2.13–2.24	2.20 2.31–2.37	<i>t</i>
[Mn(OH ₂)Br ₂ (C ₁₄ H ₁₀ N ₂)]	Mn(N ₂)Br ₂ (OH ₂)	2.27		<i>u</i>
[Mn(OH ₂) ₂ (O ₄ C ₆ H ₅) ₂]	MnO ₄ (OH ₂) ₂	2.17	2.12–2.28	<i>v</i>

^a S. Richards, B. Pederson, J. V. Silverton, and J. L. Heard, *Inorg. Chem.*, 1964, **3**, 27; edta = ethylenediaminetetraacetate. ^b Ref. 6. ^c Ref. 11; O₂C₆H₅ is citrate. ^d Ref. 8. ^e Ref. 12; O₂C₆H₄ is malate. ^f Ref. 9. ^g A. Zalkin, J. D. Forrester, and H. Templeton, *Inorg. Chem.*, 1964, **3**, 529. ^h Z. M. El Saffar and G. M. Brown, *Acta Cryst.*, 1971, **B27**, 66. ⁱ S. J. Jensen and P. Anderson, *Acta Chem. Scand.*, 1962, **16**, 1890. ^j S. J. Jensen, *Acta Chem. Scand.*, 1964, **18**, 2085. ^k S. J. Jensen, *Acta Chem. Scand.*, 1967, **21**, 889. ^l S. J. Jensen, *Acta Chem. Scand.*, 1968, **22**, 641. ^m S. J. Jensen, *Acta Chem. Scand.*, 1968, **22**, 647. ⁿ W. Schneider, *Acta Cryst.*, 1961, **14**, 784. ^o H. Montgomery, R. V. Chastain, and E. C. Lingafelter, *Acta Cryst.*, 1966, **20**, 731. ^p M. D. Glick and L. F. Dahl, *Inorg. Chem.*, 1966, **5**, 289; O₅C₅ is croconate. ^q T. Lis and B. Jezowska-Trzebiatowska, *Acta Cryst.*, 1977, **B33**, 2112. ^r Ref. 3; O₄C₄H₇ is hydrogenmaleate. ^s Ref. 5. ^t N. Milinski, B. Ribar, Z. Culum, and S. Djuric, *Acta Cryst.*, 1977, **B33**, 1678. ^u R. J. Butcher and E. Sinn, *J.C.S. Dalton*, 1976, 1186; C₁₄H₁₀N₂ is 2-(2-pyridyl)quinoline. ^v J. W. Bats, A. Kalle, and H. Fuess, *Acta Cryst.*, 1978, **B34**, 1705; O₄C₆H₅ is hydrogenphthalate.

(2) (1 859 Å³) respectively. Similarly, the *p*-chloro-substituent on the phenyl ring in (2) and (4) results in a slight increase in the *a* and *b* parameters and in the cell volume {67 Å³ [(1) to (2)] and 69 Å³ [(3) to (4)]}. A similar argument may be used with the magnesium(II) compounds.

The diffractometer pattern for the second modification of cobalt(II) *p*-chlorophenoxyacetate (7) is also listed in SUP 22870 and confirms that (4) and (7) are crystallographically different and correspond to two distinct compounds. Chemical analysis indicates that (7) is a tetrahydrate meaning that this form could either be similar to tetra-aquabis(phenoxyacetato)nickel(II)¹⁷ or that it is a dihydrated form of (4). Differential thermal

analysis showed that loss of two water molecules occurred at low temperature (*ca.* 50 °C) while the remaining two molecules were removed in a one-step process over the temperature range 100–125 °C. Elemental analysis of the powdered sample used for the X-ray powder diffractometry was consistent with a dihydrate, which emphasizes the ease of removal of the lattice water even at room temperature. Verification that the mode of complexation in (7) is similar to

that found in (4) is, however, dependent on an X-ray structure determination when suitable crystals are available. The authors wish to thank the American Cancer Society and the Institute for Cancer Research, Philadelphia for support and the University of Queensland and the Queensland Institute of Technology for the use of facilities. Two of us (G. S. and E. J. O'R) also thank the Queensland Institute of Technology for the leave to work on this project.

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