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# Metal–Phenoxyalkanoic Acid Interactions.
# Part 7. The X-Ray Crystal and Molecular Structures of Pentaaqua-(2,4,5-trichlorophenoxyacetato)manganese(II)(2,4,5-trichlorophenoxyacetate), and Pentaaqua-(2,4,5-trichlorophenoxyacetato)magnesium(II)(2,4,5-trichlorophenoxyacetate)

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*The room temperature crystal structure of the complex species of empirical formula* $Mn(II)(2,4,5\text{-}T^{**})_2(H_2O)_5$, *(1) has been determined by X-ray diffraction from diffractometer data and refined by least squares to* R *0.101 using 964 observed reflections. The crystals are triclinic, space group* $P\bar{1}$ *with* Z = 2 *in a cell of dimensions* a = *23.122(8),* b = *7.560(2),* c = *7.066(2)* Å, $\alpha = 90.72(2)$, $\beta = 86.37(2)$, $\gamma = 88.98(2)°$. *The complex units have a distorted octahedral coordination comprising five waters [Mn–O, 2.21(2) Å, mean] and one oxygen from a unidentate 2,4,5-T ligand [Mn–O, 2.07(2) Å]. Charge balance in the complex is maintained by the presence of the second 2,4,5-T anion which is fixed in the structure by hydrogen bonding and* $\pi$–$\pi$ *interactions with the ligand anions. On the basis of chemical analysis, single crystal and powder X-ray diffraction data, the Mg(II) complex (2) of the same empirical formula has been proved isostructural and isomorphous with* $[Mn(2,4,5\text{-}T)(H_2O)_5]$ *(2,4,5-T). The triclinic crystals have the cell dimensions* a = *23.00(7),* b = *7.54(2),* c = *7.07(2)* Å, $\alpha = 90.0(3)$, $\beta = 86.4(1)$, $\gamma = 88.8(1)°$.

## Introduction

A systematic structural investigation of metal(II) complexes of the phenoxyalkanoic acid analogues, which include the commercial auxin herbicides 2,4-dichlorophenoxyacetic acid [2,4-D], 2,4,5-trichlorophenoxyacetic acid [2,4,5-T] and 4-chloro-2-methylphenoxyacetic acid [MCPA] has shown a diversity of complexing modes [1–6]. The reaction of 2,4,5-T acid in aqueous ethanol with manganese(II) carbonate results in two different compounds. The product which crystallizes late from the reaction mixture has been shown by X-ray diffraction to have the formula *trans*-$[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot 2(2,4,5\text{-}TH)$ with adducted 2,4,5-T acid molecules linked to the uncoordinated carboxyl oxygens of the bonded 2,4,5-T ligands *via* strong hydrogen bonds [O···O, 2.46 Å] [4]. Another product (1) (the compound of this report), which forms initially from the reaction mixture, analysed as $[Mn(2,4,5\text{-}T)_2(H_2O)_5]$. It was expected to have the 'normal' bis-unidentate carboxylate co-ordination as found for Mn(II) in the adducted complex but this was not the case in this analysis. Attempts to prepare the *bis*-(2,4,5-T) complex have so far been unsuccessful.

The magnesium(II) complex of 2,4,5-T, prepared from magnesium carbonate in the same way as for (1), provided colourless crystals and elemental analysis suggested the formula $Mg(2,4,5\text{-}T)_2(H_2O)_5$, (2) indicating it was isostructural with the Mn(II) analogue. Two other examples of isostructural Mn(II) and Mg(II) phenoxyacetates are known, (phenoxyacetic acid and *p*-chlorophenoxyacetic acid) [2]. The single crystal X-ray structure determination of (1) was therefore completed while single crystal and powder diffractometry was used to confirm that (2) was both isomorphous and isostructural with (1). A third product (3) was obtained as white crystals by repeating the reaction procedure for (2) in 95% ethanol. The crystals immediately turned opaque when removed from the ethanol, suggesting the loss of molecules of solvation. Powder diffractometry confirmed that (2) and (3) were different.

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**2,4,5-T ≡ 2,4,5-trichlorophenoxyacetate.

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TABLE I. Atomic Coordinates ($\times 10^4$) for $C_{16}H_{18}Cl_6MnO_{11}$. Molecules A and B are the Anionic and Bonded 2,4,5-trichlorophenoxyacetate Molecules Respectively.

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Mn | 551(2) | 2350(6) | 8093(8) |
| Ow(1) | 1030(8) | 2001(25) | 5359(30) |
| Ow(2) | −106(8) | 625(23) | 6876(30) |
| Ow(3) | 17(8) | 2372(23) | 10841(31) |
| Ow(4) | 1146(8) | 4348(23) | 9191(29) |
| Ow(5) | 13(8) | 4535(22) | 7172(31) |

| | Molecule A | | | Molecule B | | |
|---|---|---|---|---|---|---|
| | *x/a* | *y/b* | *z/c* | *x/a* | *y/b* | *z/c* |
| Cl(2) | 7317(4) | −1589(11) | 4876(15) | 2617(4) | −6122(10) | 10189(14) |
| Cl(4) | 5328(4) | 1714(13) | 3389(15) | 4656(3) | −3368(13) | 11642(14) |
| Cl(5) | 5938(4) | 5391(12) | 3803(15) | 4125(3) | 458(12) | 11195(14) |
| C(1) | 7186(14) | 1935(42) | 4659(44) | 2791(13) | −2571(35) | 10428(39) |
| C(2) | 6952(13) | 363(37) | 4469(40) | 3032(12) | −4272(35) | 10537(38) |
| C(3) | 6354(13) | 248(37) | 3996(42) | 3617(13) | −4492(38) | 10927(41) |
| C(4) | 6033(14) | 1812(42) | 3953(44) | 3956(12) | −3058(37) | 11124(40) |
| C(5) | 6284(13) | 3427(37) | 4017(39) | 3745(12) | −1405(37) | 11096(40) |
| C(6) | 6885(13) | 3609(39) | 4511(42) | 3125(13) | −1076(37) | 10662(40) |
| O(7) | 7775(8) | 1848(21) | 5035(24) | 2212(8) | −2531(22) | 10007(24) |
| C(8) | 8073(12) | 3598(36) | 5174(39) | 1986(12) | −725(37) | 9961(40) |
| C(9) | 8693(13) | 3155(44) | 5892(43) | 1328(13) | −911(37) | 9370(40) |
| O(10) | 8849(7) | 1560(22) | 6012(24) | 1104(8) | −2311(24) | 9027(26) |
| O(11) | 8967(9) | 4507(27) | 6054(28) | 1109(8) | 681(23) | 9439(30) |
| H(3) | 6374 | −1026 | 4262 | 3824 | −5675 | 11119 |
| H(6) | 7149 | 4755 | 4131 | 2964 | 271 | 10412 |
| H(81) | 8047 | 3050 | 3941 | 2128 | −775 | 8758 |
| H(82) | 7951 | 3857 | 6608 | 1968 | −355 | 11370 |

## Experimental

### *(a) Preparation of Complexes*

Both compounds (1) and (2) were prepared by reaction of an aqueous ethanolic solution of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) with excess metal carbonate as previously described [4]. Elemental analysis gave the following: For (1), Found: C, 29.5; H, 2.81, Cl, 32.2%. Calc. for $Mn(2,4,5\text{-}T)_2(H_2O)_5$: C, 29.4; H, 2.77; Cl, 32.5%. For (2), Found: C, 30.6; H, 2.97; Cl, 34.1%. Calc. for $Mg(2,4,5\text{-}T)_2(H_2O)_5$: C, 30.9; H, 2.92; Cl, 34.2%. Crystals of (1) and (2) suitable for X-ray analysis were grown from aqueous ethanol as large colourless plate needles.

When the reaction procedure for the magnesium compound was repeated in 95% ethanol another dense crystalline product was formed (3) which immediately turned opaque white when isolated from the solution. Chemical analysis of the air-dried product indicated a penta-hydrate [Found: C, 30.9; H, 2.93; Cl, 33.6%] and subsequent recrystallization of this product from hot 50% ethanol/water gave crystals of (2) [confirmed by single crystal X-ray analysis]. This suggests that (3) could be an unstable $Mg(2,4,5\text{-}T)_2(H_2O)_5$ ethanol adduct.

### *(b) Crystal Data*

(1) $C_{16}H_{18}Cl_6MnO_{11}$, $M = 654.0$, triclinic, space group $P\bar{1}$, $a = 23.122(8)$, $b = 7.560(2)$, $c = 7.066(2)$ Å, $\alpha = 90.72(2)$, $\beta = 86.37(2)$, $\gamma = 88.98(2)°$, $V = 1232.4$ Å$^3$, $Z = 2$, $D_c = 1.76$ g cm$^{-1}$, $D_f = 1.75$ g cm$^{-1}$, $F(000) = 658$, $\mu(\text{Mo-}K\alpha) = 12.63$ cm$^{-1}$.

(2) $C_{16}H_{18}Cl_6MgO_{11}$, $M = 622.3$, triclinic, space group $P\bar{1}$, $a = 23.00(7)$, $b = 7.54(2)$, $c = 7.07(2)$ Å, $\alpha = 90.0(3)$, $\beta = 86.4(1)$, $\gamma = 88.8(1)°$, $V = 1223.4$ Å$^3$, $Z = 2$, $D_c = 1.69$ g cm$^{-3}$, $D_f = 1.66$ g cm$^{-3}$.

### *(c) Collection of X-ray Data and Structure Solution*

2252 reflections (1775 unique) were collected from one crystal (0.60 × 0.23 × 0.38 mm) mounted about the *c* (prism) axis on a Hilger and Watts four-circle diffractometer ($2\theta_{max} = 43°$; Zr filter; Mo-$K\alpha$ radiation, $\lambda = 0.7107$ Å). Of these 964 with $I > 2\sigma(I)$ were considered observed and used in structure refinement. Intensity statistics [mean$|E^2 - 1| = 0.824$] were indicative of a centrosymmetric structure but neither multi-solution $\Sigma_2$ sign expansion nor

TABLE II. Anisotropic Thermal Parameters[a] (Å$^2$, ×10$^3$).

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Mn | 19(3) | 12(3) | 84(5) | 7(3) | −9(3) | −1(2) |
| Ow(1) | 60(17) | 47(17) | 86(20) | 12(15) | 17(14) | −34(13) |
| Ow(2) | 22(14) | 36(15) | 97(22) | 0(14) | −23(14) | −2(11) |
| Ow(3) | 53(16) | 27(13) | 80(20) | −17(13) | −28(15) | 22(11) |
| Ow(4) | 36(16) | 33(13) | 58(20) | −5(14) | −27(14) | −6(11) |
| Ow(5) | 38(16) | 23(13) | 105(22) | 39(14) | −19(14) | −1(11) |
| O(11) | 83(15) | 22(13) | 118(21) | −3(14) | −49(14) | 10(11) |
| | | | Molecule A | | | |
| Cl(2) | 72(8) | 37(6) | 148(11) | 9(7) | −39(7) | −1(5) |
| Cl(4) | 19(7) | 103(9) | 139(11) | 14(8) | −33(7) | −20(6) |
| Cl(5) | 43(7) | 71(7) | 130(10) | 27(7) | −32(6) | 14(6) |
| | | | Molecule B | | | |
| Cl(2) | 61(6) | 32(6) | 124(10) | 10(6) | −34(6) | 2(5) |
| Cl(4) | 106(8) | 106(8) | 115(10) | 9(7) | −29(4) | 24(6) |
| Cl(5) | 76(7) | 76(7) | 114(10) | 14(7) | −18(6) | −16(6) |

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

TABLE III. Interatomic Distances (Å) and Angles (degrees).

a. Coordination sphere

| | | | |
|---|---|---|---|
| Mn–O(11B) | 2.07(2) | Mn–Ow(3) | 2.23(2) |
| Mn–Ow(1) | 2.18(2) | Mn–Ow(4) | 2.22(2) |
| Mn–Ow(2) | 2.23(2) | Mn–Ow(5) | 2.18(2) |
| O(11B)–Mn–Ow(1) | 92.9(8) | Ow(1)–Mn–Ow(5) | 94.5(8) |
| O(11B)–Mn–Ow(2) | 106.2(7) | Ow(2)–Mn–Ow(3) | 88.6(7) |
| O(11B)–Mn–Ow(3) | 85.3(8) | Ow(2)–Mn–Ow(4) | 173.1(7) |
| O(11B)–Mn–Ow(4) | 80.6(7) | Ow(2)–Mn–Ow(5) | 85.1(7) |
| O(11B)–Mn–Ow(5) | 167.0(8) | Ow(3)–Mn–Ow(4) | 91.5(7) |
| Ow(1)–Mn–Ow(2) | 85.3(8) | Ow(3)–Mn–Ow(5) | 88.6(7) |
| Ow(1)–Mn–Ow(3) | 172.9(7) | Ow(4)–Mn–Ow(5) | 88.1(7) |
| Ow(1)–Mn–Ow(4) | 95.1(7) | | |

b. Intraligand

| | Molecule A | Molecule B |
|---|---|---|
| C(1)–C(2) | 1.32(4) | 1.40(4) |
| C(2)–C(3) | 1.45(4) | 1.41(4) |
| C(2)–Cl(2) | 1.72(2) | 1.73(3) |
| C(3)–C(4) | 1.39(4) | 1.36(4) |
| C(4)–C(5) | 1.36(4) | 1.33(4) |
| C(4)–Cl(4) | 1.70(3) | 1.70(3) |
| C(5)–C(6) | 1.46(4) | 1.50(4) |
| C(5)–Cl(5) | 1.69(3) | 1.68(3) |
| C(6)–C(1) | 1.44(4) | 1.40(4) |
| C(1)–O(7) | 1.40(4) | 1.39(4) |
| O(7)–C(8) | 1.51(3) | 1.46(3) |

*(continued overleaf)*

TABLE III. *(continued)*

| | Molecule A | Molecule B |
|---|---|---|
| C(8)–C(9) | 1.58(4) | 1.61(4) |
| C(9)–O(10) | 1.26(4) | 1.21(3) |
| C(9)–O(11) | 1.22(4) | 1.30(3) |
| | | |
| C(2)–C(1)–C(6) | 125(3) | 121(3) |
| C(2)–C(1)–O(7) | 113(3) | 114(2) |
| C(6)–C(1)–O(7) | 121(3) | 125(2) |
| C(1)–C(2)–C(3) | 120(3) | 120(3) |
| C(1)–C(2)–Cl(2) | 123(3) | 121(2) |
| C(3)–C(2)–Cl(2) | 117(3) | 119(2) |
| C(2)–C(3)–C(4) | 118(3) | 120(3) |
| C(3)–C(4)–C(5) | 122(3) | 122(3) |
| C(3)–C(4)–Cl(4) | 119(2) | 119(2) |
| C(5)–C(4)–Cl(4) | 118(2) | 118(2) |
| C(4)–C(5)–C(6) | 121(3) | 120(3) |
| C(4)–C(5)–Cl(5) | 125(2) | 127(2) |
| C(6)–C(5)–Cl(5) | 113(2) | 113(2) |
| C(5)–C(6)–C(1) | 113(3) | 116(3) |
| C(1)–O(7)–C(8) | 116(2) | 111(2) |
| O(7)–C(8)–C(9) | 106(2) | 105(2) |
| C(8)–C(9)–O(10) | 119(3) | 124(3) |
| C(8)–C(9)–O(11) | 110(3) | 106(2) |
| O(10)–C(9)–O(11) | 130(3) | 130(3) |
| C(9)–O(11)–Mn | 142(2) | – |

the TANG direct methods of SHELX [7] provided a solution. The structure was solved by origin relocation in space group $P1$ using a recognizable molecular fragment from one of the E-maps. The remainder of the heavy atoms were located in $P\bar{1}$ and full-matrix least-squares refinement with anisotropic thermal parameters for manganese, chlorines and the co-ordinated oxygens only, reduced $R$ $[=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|]$ to 0.101 and $R_w$ $[=\Sigma w(\|F_o|-|F_c\|^2/\Sigma|F_o|^2)^{1/2}]$ to 0.088. A value of $w = 2.50/[\sigma^2(F_o) + 4.9 \times 10^{-4} (F_o)^2]$ was used. Most hydrogens of the 2,4,5-trichlorophenoxyacetato groups were located in a difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic thermal parameters ($U$) set invariant at 0.05 Å$^2$. Four intense low-angle reflections (−1, −1, 2; −2, −2, 3; 0, −2, 3; −1, 3, 3) were considered to be affected by extinction and were removed before the final refinement cycle. No corrections were made for absorption. The maximum peak in the final difference-Fourier was 0.30 eÅ$^{-3}$. Scattering factors used were those of Cromer and Mann (non hydrogens) [8] and Stewart, Davidson and Simpson (hydrogens) [9]. Final atomic positional and anisotropic thermal parameters are listed in Tables I and II while bond distances and angles are given in Table III.

### *(d) Powder Diffractometry*

X-ray powder diffraction patterns for the compounds were recorded at 298 K on a Philips PW 1140 powder diffractometer using a LiF crystal analyzer and Co-$K\alpha$ radiation ($\lambda$ = 1.7889 Å). Indexing of the patterns for (1) and (2) were completed using the accurate cell parameters from the single crystal analysis of (1) and accurate cell parameters for (2) were then obtained by least-squares refinement of angle data from the diffraction pattern using 12 reflections in the $2\theta$ range 4–41°. Indexed diffraction patterns are available from the authors.

## Discussion

The title compound provides the first recorded example of a complex having the same carboxylate species both coordinate and ionic. The coordination about Mn(II) consists of five waters [Mn–O, 2.21(2) Å mean] and one oxygen [Mn–O, 2.07(2) Å] from a unidentate 2,4,5-T ion (B) giving a considerably distorted octahedron (Fig. 1). Angles, particularly those associated with the carboxylate oxygen [O(11)] deviate by up to 16° from the regular values [O(11)–Mn–Ow(2), 106.2(7)°; O(11)–Mn–Ow(5), 167.0(8)°]. The charge on the complex unit is balanced by the second 2,4,5-T anion (A) which layers in the structure almost parallel to the (B) ligands, (dihedral angle, 0.90°), separated from them by *ca.* $c/2$ (3.53 Å) (Fig. 2). The corresponding inter-ring separation (coordinated to adducted) for the

TABLE IV. Comparative Torsion Angles (degrees) about the Oxoacetic Axis Side-chain for Molecule A (ionic) and Molecule B (coordinated) for (1), for Coordinated (C) and Adducted (D) 2,4,5-T Molecules in $[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot2(2,4,5\text{-}TH)$ [4], and un-coordinated 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-TH) [11].

| | A | B | C | D | 2,4,5-TH |
|---|---|---|---|---|---|
| C(2)–C(1)–O(7)–C(8) | +177 | +179 | +173 | −175 | +174 |
| C(1)–O(7)–C(8)–C(9) | +172 | +178 | +177 | +179 | −172 |
| O(7)–C(8)–C(9)–O(11) | +180 | +176 | +170 | −176 | +180 |
| C(8)–C(9)–O(11)–Mn | – | +143 | −65 | – | – |

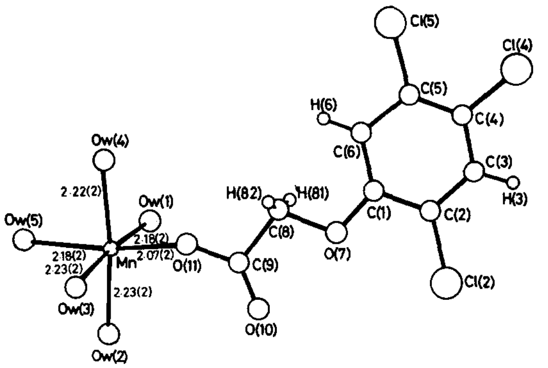

Fig. 1. Molecular conformation and atom number scheme for the $[Mn(2,4,5\text{-}T)(H_2O)_5]^+$ complex unit.

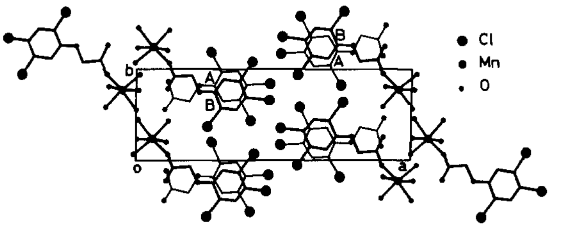

Fig. 2. Perspective view of the packing in the cell perpendicular to *ab*.

$[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot2(2,4,5\text{-}TH)$ structure is 3.59 Å [4]. The presence of π–π interactions between the benzene rings in both structures must be considered of importance in stabilizing the 2,4,5-T molecules in the solid state. Similar inter-ring separations are found in the isostructural phenanthroline adducts, $[Ba(phen)_2(H_2O)_4]\cdot2phen$, (3.516 Å) and $[Sr(phen)_2(H_2O)_4]\cdot2phen$ (3.534 Å) [10].

Hydrogen bonding between both (A) carboxyl oxygens [O(10)A–Ow(1), 2.85 Å; O(10)A–Ow(2), 2.62 Å, O(11)A–Ow(1), 2.83 Å; O(11)A–Ow(5), 2.59 Å] also helps to fix the anion in the structure. Additional intermolecular hydrogen bonding between the water ligands exists, *e.g.* Ow(1) (2 contacts, 2.81, 2.81 Å); Ow(3) (1 contact, 2.71 Å) while a very short contact (2.53 Å) is found between the un-coordinated carboxyl oxygen of the B molecule [O(10B) and Ow(4) of an adjacent complex unit. This hydrogen bonding is probably responsible for the angular distortion associated with O(11)B in the coordination octahedron.

Both ligand and anionic 2,4,5-T species are conformationally similar and similar to the planar, 2,4,5-T acid (Table IV) [11]. Structural features retained include the discrete angular differences between C–C–O (hydroxyl) and C–C–O (carbonyl) which allows side-chain conformation classification as *synplanar-synplanar* (carbonyl), the conformation of the parent acid [10] and all known phenoxyacetic acids [12] and their complexes [1–6]. The packing of the adducted complex $[Mn(2,4,5\text{-}T)_2(H_2O)_4]\cdot2(2,4,5\text{-}TH)$ and (1) in their respective triclinic unit cells is very similar. Bonding of the carboxyl group to Mn(II) should be preferred to the existence of free anionic species [as is evidenced in the short Mn–O(carboxyl) distance (2.07 Å)], and it is suggested that strong orientation tendencies exist in consideration of the packing of the 2,4,5-T ions or molecules in this system and bonding interactions may be of lesser consequence. It would therefore appear that in the presence of stoichiometric proportions of Mn(II) and 2,4,5-T, in ethanol/water, the major reaction product would be (1) while in the presence of an excess of 2,4,5-T, the adducted species would be favoured. Furthermore, under the same reaction conditions, Mg(II) forms the isomorphous and isostructural $[Mg(2,4,5\text{-}T)(H_2O)_5]$ (2,4,5-T) species (2). The preference for formation of (2) is evident in the reversion of the ethanol solvated compound (3) to (2) on recrystallization from aqueous ethanol. Although isostructural Mg(II) and Mn(II) carboxylates are not common, two examples have been found in the phenoxyacetate and *p*-chlorophenoxyacetate complexes of these metals [2]. However, the mode of coordination is different from that of the present example, with the carboxylate groups bridging metal centres giving a two-dimensional polymer structure of the type *trans*-$[M(II)(phenoxy)_2(H_2O)_2]_n$. The unidentate coordination in compound (2) is by far the most common type found among the few known examples of Mg carboxylates. With the exception of the monocapped trigonal prismatic coordination about Mg in the complex $Na_2[Mg(H_2O)(edta)] \cdot 5H_2O$ [13, 14], and the pentagonal bipyramidal anion in $[Mg(H_2O)_6][Mg(H_2O)_3(edta)]$ [15, 16], all are octahedral monomeric structures, *e.g.* tetraaquabis(4-chloro-2-methylphenoxyacetato)magnesium(II) dihydrate [5], tetraaqua(*S*-malato)magnesium(II) hydrate [17, 18], diaquabis(hydrogenmalonato)magnesium(II) [19] and diaquabis(pyridine-2-carboxylato)magnesium(II) [20].

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