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Metal–Phenoxyalkanoic Acid Interactions
Part 10. Crystal and Molecular Structures of catena-[Tetraaqua(4-carboxylato-phenoxyacetato)manganese(II)], Tetraaquabis(4-carboxyphenoxyacetato)nickel(II) and Tetraaquabis(4-carboxyphenoxyacetato)cobalt(II)

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The crystal structures of two metal(II) complexes of 4-carboxyphenoxyacetic acid have been determined by X-ray methods. The first, catena[tetraaqua(4-carboxylato-phenoxyacetato)manganese(II), (1) forms crystals which are orthorhombic, space group Pbca, with 8 molecules in a unit cell of dimensions a = *10.356(2),* b = *9.086(2),* c = *25.673(8) Å. It has a polymeric structure involving both* cis-*related carboxylate groups and four water molecules about a slightly distorted octahedron. The mean Mn–O (water) distance is 2.214(7) Å, while the Mn–O (carboxylate) distances are 2.147(6) and 2.111(7) Å. Tetraaquabis(4-carboxyphenoxyacetato)nickel(II) (2) is triclinic, space group* $P\bar{1}$ *with one molecule in the cell, dimensions* a = *4.896(2),* b = *5.679(2),* c = *18.403(6) Å,* α = *93.75(3),* β = *91.78(3),* γ = *95.76(2). The centrosymmetric complex units are discrete monomers with unidentate* trans-*related acid ligands bonded through the phenoxy carboxylate oxygen [Ni–O, 2.058(3) Å]. The Ni–O (water) distance is 2.055(4) Å. Single crystal diffractometry and elemental analysis have been used to prove that the Co(II) (3) analogue is isomorphous and isostructural with the Ni(II) complex. The p-carboxy group of one molecule is hydrogen bonded about a centre of symmetry to another p-carboxy group.*

Introduction

The X-ray structures of a number of divalent metal complexes of phenoxyalkanoic acids have already been described [1–9]. These acids include the commercial herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 4-chloro-2-methylphenoxyacetic acid (MCPA). The complexes have a diversity of stereochemistries. The current investigation deals with the ligand, 4-carboxyphenoxyacetic acid, PCPA, which has a second potential donor group for complexation. The interest in this ligand lies in whether: a) both carboxylic acid groups are involved in complexation; b) the phenoxy carboxylic acid has an involvement in coordination or c) if there is a tendency for the metal ion and ligand to form discrete cation-anion interactions. This is found in Mn(II), Mg(II), Ni(II) sulphates where the metal ion is in a $[M(H_2O)_6]^{2+}$ octahedron. Examples of complex anions are less well known, but does occur with the isomorphous and isostructural series of metal(II) *p*-hydroxybenzoates [10], where metal(II) = Mg, Co, Ni, Zn, and is known for cobalt(II) hydrogenphthalate hexahydrate [11].

Chemical analysis for the manganese(II) complex suggested the formula $[Mn(PCPA)(H_2O)_4]$. The PCPA ligand could cause a polymeric structure involving both carboxylate groups. This is consistent with manganese(II) carboxylate structures where polymers

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TABLE I. Experimental Data for the X-ray Study of $[Mn(PCPA)(H_2O)_4]_n$, (*1*) and $[NiPCPA)_2(H_2O)_4]$, (*2*).

	(*1*)	(*2*)
A. Crystal Parameters at 25 °C		
Formula:	$C_9H_{14}MnO_9$	$C_{18}H_{22}NiO_{14}$
Mol. wt.:	321.1	521.1
Crystal system:	orthorhombic	triclinic
Space group:	$Pbca(D_{2h}^{15}$, No. 61)	$P\bar{1}(C_i^1$, No. 2)
Cell dimensions:	a = 10.356(2)	4.896(2) Å
	b = 9.086(2)	5.679(2)
	c = 25.673(8)	18.403(6)
	α = 90	93.75(3)°
	β = 90	91.78(3)
	γ = 90	95.76(2)
Volume:	2416	508 $Å^3$
Z:	8	1
ρ(calc.):	1.76	1.70 g cm^{-3}
ρ(found):	1.77	1.69 g cm^{-3}
F(000):	1320	270
μ(Mo Kα):	11.9	10.4 cm^{-1}
B. Measurement of Data, Structure Solution and Refinement		
Diffractometer:	Enraf–Nonius CAD-4	
Radiation:	Graphite monochromated Mo Kα (λ = 0.7107 Å)	
Crystal Size:	0.40 × 0.30 × 0.08 mm	0.10 × 0.10 × 0.50 mm
Reflections collected:	2390	2008
2θ max.:	50°	50°
Reflections used:	$991[>2.0\sigma(I)]$	$1160[>2.5\sigma(I)]$
Structure solution:	Direct methods (SHELX) [14]	Heavy atom method
Final R:	0.056	0.046
Final R_w:	0.045	0.044
w:	$1.63/(\sigma^2 F_o + 0.003 F_o^2)$	$1.19/(\sigma^2 F_o + 0.003F_o^2)$

predominate. In fact phenoxyalkanoates provide two examples, manganese phenoxyacetate di-hydrate [2] and a polymorph of manganese 2,4,5-trichlorophenoxyacetate [9].

In contrast, both nickel and cobalt complexes gave chemical analyses consistent with a formula $[M(PCPA)_2(H_2O)_4]$. This would indicate that one of the carboxyl groups was complexed, the other remaining protonated. Consequently, the most common stereochemistry consistent with the centrosymmetric space group found for these compounds could be six-coordinate with the carboxyl groups *trans*-related. This has been found in nickel(II) phenoxyacetate [13].

Experimental

Preparation of Complexes

All complexes were prepared by treating hot aqueous neutral solution of the acid (0.01 mol) with an aqueous solution of the metal sulphate (0.01 mol). Crystals were grown from the aqueous solutions. Calc. for $C_9H_{14}MnO_9$ (*1*): C, 33.7; H, 4.39%. Found: C, 33.7; H, 4.36%. Calc. for $C_{18}H_{22}NiO_{14}$ (*2*): C, 41.5; H, 4.26%. Found: C, 41.6; H, 4.30%. Calc. for $C_{18}H_{22}CoO_{14}$ (*3*): C, 41.5; H, 4.25%. Found: C, 41.6; H, 4.30%.

Collection of X-ray Data and Structure Solution

Details regarding cell parameters, data acquisition and structure solutions for (*1*) and (*2*) are given in Table 1. The unit cell parameters and space group for the Co analogue (*3*) were determined from single crystal Weissenberg photographs. These confirmed that (*2*) and (*3*) were isostructural and isomorphous. For (*1*) and (*2*), all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were located from difference-Fourier syntheses, and in (*1*), were included in the refinement at fixed posi-

TABLE II. Atomic Coordinates for $[Mn(PCPA)(H_2O)_4]_n$, (*1*) and $[Ni(PCPA)_2(H_2O)_4]$, (*2*) [Non hydrogens, $\times 10^4$, Hydrogens, $\times 10^3$].

	x/*a*	y/*b*	z/*c*		x/*a*	y/*b*	z/*c*
(*1*) $[Mn(PCPA)(H_2O)_4]_n$							
Mn	5427(1)	1017(2)	3152.8(5)	H(11)	541	176	215
Ow(1)	5955(7)	1832(9)	2383(2)	H(12)	661	175	217
Ow(2)	6392(6)	−1059(8)	2833(3)	H(21)	612	−146	249
Ow(3)	4478(6)	3077(8)	3334(3)	H(22)	658	−180	307
Ow(4)	3550(6)	487(8)	2776(2)	H(31)	386	303	347
C(1)	8934(8)	−1250(11)	4756(3)	H(32)	482	395	350
C(2)	9779(9)	−2448(12)	4808(4)	H(41)	356	35	239
C(3)	9787(9)	−3202(12)	5275(4)	H(42)	325	130	269
C(4)	8956(8)	−2844(10)	5673(3)	H(2)	1058	−233	453
C(5)	8134(9)	−1640(12)	5616(4)	H(3)	1054	−407	531
C(6)	8097(9)	−841(13)	5154(4)	H(5)	774	−114	597
O(7)	8974(6)	−556(7)	4275(2)	H(6)	727	9	515
C(8)	7980(9)	464(12)	4153(4)	H(81)	799	129	431
C(9)	8166(9)	967(12)	3600(3)	H(82)	703	19	419
O(10)	9119(7)	604(9)	3343(2)				
O(11)	7266(6)	1792(8)	3424(2)				
C(41)	8961(9)	−3752(12)	6159(3)				
O(410)	8080(6)	−3545(7)	6496(2)				
O(411)	9822(6)	−4733(9)	6207(2)				
(*2*) $[Ni(PCPA)_2(H_2O)_4]$							
Ni	−10000	10000	10000	H(2)	−174(14)	1219(13)	776(4)
C(1)	−3425(12)	8784(10)	7381(3)	H(3)	119(12)	1279(10)	678(3)
C(2)	−1701(13)	10824(11)	7365(3)	H(5)	−132(12)	615(10)	594(3)
C(3)	152(13)	11097(12)	6824(3)	H(6)	−445(15)	562(12)	685(3)
C(4)	236(11)	9307(10)	6272(3)	H(81)	−826(13)	646(11)	759(3)
C(41)	2289(12)	9619(11)	5701(3)	H(82)	−624(13)	521(12)	805(3)
O(410)	3886(11)	11506(10)	5746(3)	H(410)	404(28)	1156(24)	544(6)
O(411)	2350(9)	7951(8)	5207(2)	Hw(11)	−593(16)	1283(14)	995(4)
C(5)	−1530(12)	7278(11)	6290(3)	Hw(12)	−750(17)	1357(15)	1044(4)
C(6)	−3399(13)	6964(12)	6834(3)	Hw(21)	−820(12)	748(11)	1098(3)
O(7)	−5129(8)	8688(7)	7958(2)	Hw(22)	−620(12)	936(10)	1089(3)
C(8)	−7021(12)	6672(10)	8004(3)				
C(9)	−8738(11)	7019(9)	8666(3)				
O(10)	−7925(7)	8707(6)	9130(2)				
O(11)	−10832(8)	5573(6)	8700(2)				
Ow(1)	−7395(9)	13006(7)	9998(2)				
Ow(2)	−7295(9)	8520(8)	10692(2)				

tions with isotropic thermal parameters (U's) set invariant at 0.05 Å^2. In (*2*), both positional parameters and isotropic thermal parameters for H were allowed to refine. Scattering factors used were those of Cromer and Mann [15] (non-hydrogens) and Stewart *et al.* [16] (hydrogens). No corrections were made for absorption or extinction. Final positional parameters are given in Table II, while structure factor amplitudes and anisotropic thermal parameters are available from the authors. Bond distances and angles are listed in Table III.

Discussion

The bonding of PCPA in complexes of Mn(II) (*1*) and Ni(II) (*2*) is considerably different (Figs. 1 and 2). In (*1*), the coordination sphere about Mn is distorted octahedrally (Fig. 1) and involves four water molecules [Mn–O range, 2.182–2.287(7) Å; mean 2.214(7) Å] and two *cis*-related carobxylate oxygens. The first carboxylate oxygen is from the oxoacetate group [Mn–O, 2.147(6) Å] while the second is from the *p*-carboxyl group of an adjacent PCPA molecule [Mn–O, 2.111(7) Å], resulting in zig-zag polymer

TABLE III. Bond Distances (Å) and Angles.

(*1*)		(*2*)	
a. Distances			
Mn–O(11)	2.147(6)	Ni–O(10)	2.058(3)
Mn–O(411)	2.111(7)	Ni–Ow(1)	2.026(4)
Mn–Ow(1)	2.182(7)	Ni–Ow(2)	2.084(4)
Mn–Ow(2)	2.287(7)		
Mn–Ow(3)	2.165(7)		
Mn–Ow(4)	2.224(6)		
C(1)–C(2)	1.404(14)		1.366(9)
C(1)–C(6)	1.390(13)		1.396(8)
C(1)–O(7)	1.387(11)		1.371(6)
C(2)–C(3)	1.382(14)		1.374(8)
C(3)–C(4)	1.374(13)		1.394(8)
C(4)–C(5)	1.395(14)		1.373(8)
C(4)–C(41)	1.496(13)		1.485(8)
C(5)–C(6)	1.391(14)		1.386(8)
O(7)–C(8)	1.421(12)		1.408(7)
C(8)–C(9)	1.503(13)		1.516(7)
C(9)–O(10)	1.233(12)		1.265(6)
C(9)–O(11)	1.279(12)		1.254(6)
C(41)–O(410)	1.272(11)		1.258(8)
C(41)–O(411)	1.267(12)		1.272(7)
b. Angles			
Ow(1)–Mn–Ow(2)	81.1(3)	Ow(1)–Ni–Ow(2)	90.8(2)
Ow(1)–Mn–Ow(3)	90.8(3)	Ow(1)–Ni–O(10)	92.9(2)
Ow(1)–Mn–O(11)	87.7(3)	Ow(2)–Ni–O(10)	88.6(1)
Ow(1)–Mn–O(411)	165.5(3)		
Ow(2)–Mn–Ow(3)	171.4(3)		
Ow(2)–Mn–Ow(4)	92.7(3)		
Ow(2)–Mn–O(11)	89.9(3)		
Ow(2)–Mn–O(411)	87.3(3)		
Ow(3)–Mn–Ow(4)	83.3(3)		
Ow(3)–Mn–O(11)	92.8(3)		
Ow(3)–Mn–O(411)	100.1(3)		
Ow(4)–Mn–O(11)	170.9(3)		
Ow(4)–Mn–O(411)	87.7(3)		
O(11)–Mn–O(411)	101.1(3)		
C(2)–C(1)–C(6)	121.8(9)		120.6(5)
C(2)–C(1)–O(7)	114.7(8)		115.5(5)
C(6)–C(1)–O(7)	123.5(9)		123.9(5)
C(1)–C(2)–C(3)	118.0(8)		120.7(6)
C(2)–C(3)–C(4)	121.6(9)		120.0(6)
C(3)–C(4)–C(5)	119.3(9)		118.7(5)
C(3)–C(4)–C(41)	119.2(8)		119.1(5)
C(5)–C(4)–C(41)	121.5(8)		122.2(5)
C(4)–C(5)–C(6)	121.0(9)		122.1(6)
C(1)–C(6)–C(5)	118.0(9)		117.8(6)
C(1)–O(7)–C(8)	118.2(7)		119.1(4)
O(7)–C(8)–C(9)	108.4(8)		109.4(4)
C(8)–C(9)–O(10)	121.8(9)		117.5(4)
C(8)–C(9)–O(11)	114.8(8)		116.0(5)
O(10)–C(9)–O(11)	123.4(9)		126.5(5)
C(4)–C(41)–O(410)	118.9(8)		117.5(5)
C(4)–C(41)–O(411)	118.2(8)		118.0(5)
O(410)–C(41)–O(411)	122.9(8)		124.4(6)

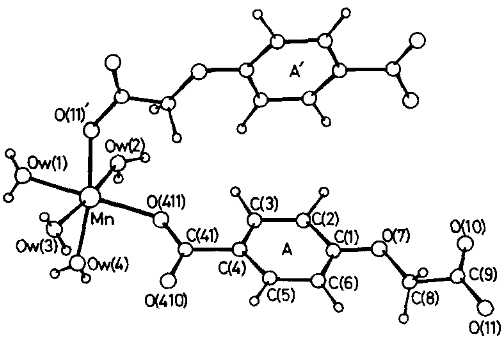

Fig. 1. Molecular configuration and atom naming scheme for $[Mn(PCPA)(H_2O)_4]_n$ (*1*). Hydrogen atoms take the name of the parent carbon or oxygen. Primed atoms are generated by the symmetry operator (½ + x, ½ – y, –z).

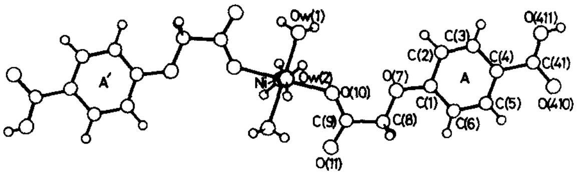

Fig. 2. Molecular configuration and atom numbering scheme for $[Ni(PCPA)_2(H_2O)_4]$ (*2*). Hydrogen atoms take the name of the attached carbon or hydrogen atom. Primed atoms are generated by the symmetry operation (–x, –y, –z).

chains down the *b* axis (Fig. 3). This arrangement forms alternate blocks of acid ligands and tetraaquamanganese centres along the *c* crystal axis. Only one other polymeric structure involving Mn(II) and a dicarboxylic acid is known, and in this case, tetraaquasuccinatomanganese(II) [17], differs from the present example with acid groups *trans*-related. Diaquabis(hydrogenphthalato)manganese(II) [12] and potassium diaquabis(oxalato)manganese(II) [18] are monomeric with the acids acting as bidentate ligands. A single hydrogen bond (2.980 Å) links the water molecule [Ow(1)] with another [Ow(4)] of an adjacent complex chain. The non-complexed oxygens of the two carboxyl groups are also hydrogen bonded to coordinated water molecules [Ow(1)···O(10), 2.887 Å; Ow(3)···O(10), 2.717 Å]; Ow(3)···O(410), 2.718 Å; Ow(4)···O(10), 2.934 Å; Ow(4)···O(410), 2.616 Å] while another interaction [2.836 Å] involving waters and coordinated carboxyl oxygens [Ow(2)···O(11)] is found.

In contrast to (*1*), the two PCPA ligands of (*2*) have only one carboxyl group (the oxoacetic acid group) participating in metal bonding [Ni–O, 2.058(3) Å] with the *p*-carboxy group being left protonated. The centrosymmetric monomeric complex units (Fig. 2) have undistorted octahedral stereochemistry with the other four coordination positions occupied by water ligands [Ni–O, 2.026, 2.084(4) Å]. Hydrogen bonding interactions link

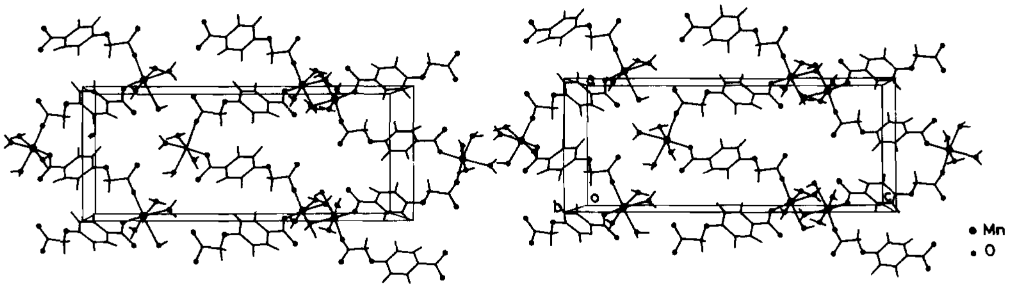

Fig. 3. Stereoview for (*1*) viewed perpendicular to *ac*.

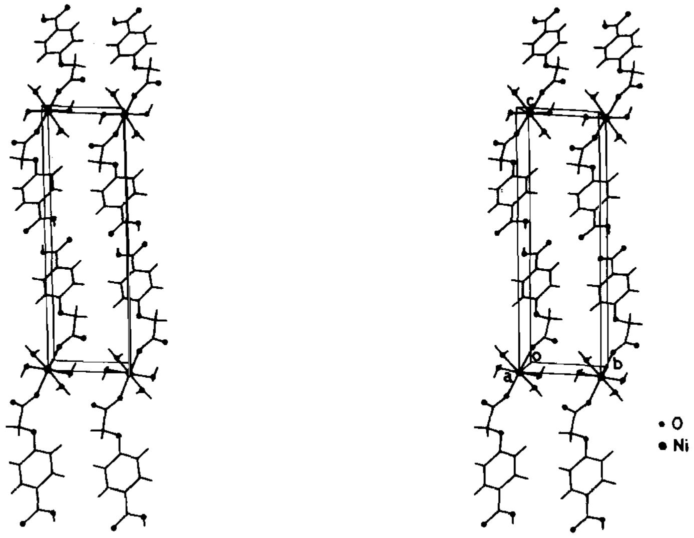

Fig. 4. Stereoview for (*2*) viewed perpendicular to *bc*.

the free carboxyl groups [O(410)···O(411)′, 2.593(4) Å] of adjacent complex units giving linear chains along the *c* crystal axis (Fig. 4). Intramolecular hydrogen bonding involving the O(10) and O(11) oxygens and the coordinated waters [O(10)··· Ow(1), 2.959 Å; O(10)···Ow(2), 2.862, 2.964 Å; O(11)···Ow(1), 2.959 Å; O(11)···Ow(2), 2.733 Å], tie the ligands into the structure (Fig. 4). In addition, intermolecular hydrogen bonding between the coordinated waters exist [Ow(1)···Ow(2), 2.841, 2.885 Å].

The PCPA ligands in both structures are similar and essentially planar (torsion angles are compared in Table IV). Bond distances and angles are comparable and similar to equivalent distances and angles found for non-coordinated phenoxy acids [19, 20] and metal complexes [1–9]. Of particular significance is that in all cases, the *exo* angles in the phenoxy carboxyl group is distorted. This occurs without exception among the free acids and in the metal complexes on removal of the proton. In all known examples of metal phenoxyacetates, the conformation of the phenoxy ligands (*synplanar-synplanar*) is preserved. This side-chain conformation has the carbonyl oxygen at a favourable interactive distance from the ether oxygen (*ca.* 2.7 Å). The C–C–O (carbonyl) angle is also larger than the C–C–O (hydroxyl) angle and this discrete angular difference is retained when the acid is de-protonated. By this means, the origin of the oxygen which is bonded to the metal may be identified as being either 'carbonyl' or 'hydroxyl'.

TABLE IV. Torsion Angles (°) about the PCPA Ligands in (*1*) and (*2*).

	(*1*)	(*2*)
O(11)–C(9)–C(8)–O(7)	+174(1)	+167(1)
C(9)–C(8)–O(7)–C(1)	−175(1)	−178(1)
C(8)–O(7)–C(1)–C(2)	+168(1)	+178(1)
C(5)–C(4)–C(41)–O(411)	−171(1)	−177(1)

In (*1*) and (*2*), the *synplanar-synplanar* conformation is retained with the oxygen bonded to the metal in (*1*) being 'hydroxyl' [C–C–O(carbonyl, 121.8(9)°; C–C–O(hydroxyl), 114.8(8)°]. In (*2*), the angle difference is less pronounced [C–C–O(carbonyl), 117.5(5)°; C–C–O(hydroxyl), 116.0(4)°] but if this conformation is retained, the bonded oxygen [O(10)] is 'carbonyl'. For (*1*) the O(7)···O(10) distance is 2.619(10) Å while for (*2*) it is 2.590(6) Å. In other examples [1–9], it is more common that the 'carbonyl' and not the 'hydroxyl' oxygen bonds to the metal. Chemical analysis and single crystal X-ray diffractometry confirmed the isostructural nature of the Ni and Co analogues [(*2*) and (*3*)].

It is common to have an isomorphous and isostructural relationship between Ni(II) and Co(II) complexes. This occurs with the analogous isomeric acid, 2-carboxyphenoxyacetic acid (OCPA) [Ni(II), Co(II), Mg(II)] [21] and 4-hydroxybenzoic acid [Ni(II), Co(II), Mg(II), Zn(II)] [10].

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