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Metal–Phenoxyalkanoic Acid Interactions.
Part 20*. The Crystal Structures of Diaquabis(2-carbamoylphenoxyacetato)-copper(II) and Tetraaquabis(2-carbamoylphenoxyacetato)nickel(II)

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Abstract

The crystal structures of two metal(II) complexes of 2-carbamoylphenoxyacetic acid (salicylamide-O-acetic acid, (SAH)) have been determined by X-ray methods. The first, diaquabis(2-carbamoylphenoxyacetato)copper(II) (**1**), forms triclinic crystals, space group $P\bar{1}$ with 1 molecule in a unit cell of dimensions $a = 4.0796(4)$, $b = 9.936(1)$, $c = 13.020(2)$ Å, $\alpha = 103.88(1)$, $\beta = 107.00(1)$, $\gamma = 97.61(1)°$. The complex units are centrosymmetric monomers involving unidentate, *trans*-related acid ligands bonded through the phenoxy carboxylate oxygen [Cu–O, 1.933(2)] with two water ligands [Cu–Ow, 1.961(3) Å] completing a square planar coordination about the central Cu(II) atom. Tetraaquabis(2-carbamoylphenoxyacetato)nickel(II) (**2**), is monoclinic, space group $P2_1/c$ with 2 molecules in a unit cell of dimensions $a = 10.957(2)$, $b = 4.996(1)$, $c = 20.042(4)$ Å, $\beta = 105.51(2)°$. These complex units are discrete centrosymmetric monomers involving unidentate, *trans*-related acid ligands bonded through the phenoxy carboxylate oxygen [Ni–O, 2.072(2) Å] with four water ligands [Ni–Ow (mean), 2.069(2) Å] completing an almost regular octahedral coordination around the central Ni(II) atom. In both complexes, inter and intramolecular hydrogen bonding aids complex and crystal lattice stability.

Introduction

A systematic study of the interaction of divalent metal ions with 2-substituted phenoxyalkanoic acids has been initiated following the observation of some unusual interactive modes of 2-chlorophenoxyacetic acid with divalent copper and nickel [2, 3]. Complexes of 2-nitrophenoxyacetic acid [4] and 2-formylphenoxyacetic acid [5] are relatively stereotypical, in contrast to the two copper(II) 2-carboxyphenoxyacetate polymorphs. In polymorph (A), $[Cu(OCPA)(H_2O)]_n$, the *ortho*-carboxyl group is involved in coordination with copper, giving a square pyramidal step-polymer structure bridged through the same group. The remaining positions of the coordination sphere are occupied by the ether and carboxyl oxygens of the oxoacetate side-chain with the water molecule axially located [1]. The second polymorph, (B) $[Cu(OCPAH)_2(H_2O)_2]$ obtained later in the crystallization, is square planar with *trans*-related unidentate phenoxy carboxylates, while the protonated 2-carboxyl groups form cyclic hydrogen bonded links with adjacent complex units. This paper reports the crystal structures of the copper(II) and nickel(II) complexes with 2-carbamoylphenoxyacetic acid (SAH), $[Cu(SA)_2(H_2O)_2]$ (**1**) and $[Ni(SA)_2(H_2O)_4]$ (**2**).

Experimental

Preparation

Both complexes (**1**) and (**2**) were prepared by reacting the ligand, 2-carbamoylphenoxyacetic acid (SAH) in aqueous ethanol with a suspension of excess metal carbonate (in aqueous ethanol) and digesting for 1 h at 70–90 °C. The excess carbonate was removed by filtration. The filtrate on standing at room temperature, yielded crystals which were recrystallised from absolute ethanol. *Anal.* For (**1**), found: C = 44.6, H = 4.11%; calc. for $C_{18}H_{20}CuN_2O_{10}$: C = 44.3, H = 4.10. For (**2**), found C = 41.7, H = 4.62%; calc. for $C_{18}H_{24}NiN_2O_{12}$: C = 41.6, H = 4.62%.

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TABLE I. Cell Data for $[Cu(SA)_2(H_2O)_2]$ (1) and $[Ni(SA)_2(H_2O)_4]$ (2)

	(1)	(2)
Formula	$C_{18}H_{20}CuN_2O_{10}$	$C_{18}H_{24}NiN_2O_{12}$
M_r	487.9	519.3
a (Å)	4.0796(4)	10.957(2)
b (Å)	9.936(1)	4.996(1)
c (Å)	13.020(2)	20.042(4)
α (°)	103.88(1)	–
β (°)	107.00(1)	105.51(2)
γ (°)	97.61(1)	–
V (Å^3)	478.2(1)	1057.2(4)
ρ_c (g cm^{-3})	1.694	1.631
ρ_f (g cm^{-3})	1.708	1.636
Z	1	2
μ (cm^{-1})	12.03	9.86
F(000)	251	540
Space group	$P\bar{1}$	$P2_1/c$
Data collection		
Diffractometer	Nicolet R3m	Nicolet R3m
Radiation	Mo Kα	Mo Kα
$2\theta_{max}$ (°)	46	45
Unique reflections measured	1333	1383
Crystal dimensions (mm)	0.26 × 0.18 × 0.08	0.22 × 0.16 × 0.10
Structure solution and refinement		
Method used	heavy atom	heavy atom
R	0.037	0.028
R_w	[b]	0.029
w[a] A	–	1.74
B	–	1.76×10^{-4}
Data used	1259	1165
Discrimination	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$

[a] $w = A/[\sigma^2F_o + BF_o^2]$. [b] Unit weights used.

Crystal Data, X-ray Data Collection and Structure Refinement

Table I contains details of unit cell parameters, data acquisition and structure solution for (1) and (2). Data were processed using the profile fitting procedure of Diamond [6] while the structures were solved by the heavy-atom method using the SHELX-76 program set [7]. For (1) and (2), all non-hydrogens were refined with anisotropic thermal parameters. Hydrogens were located from difference-Fourier syntheses and were included in the refinement at fixed positions with isotropic thermal parameters (U) set invariant at 0.05 Å^2. Neutral atom scattering factors were used [8] and corrections were made where appropriate for the effects of anomalous dispersion [8]. No corrections were made for absorption or extinction. Final positional parameters are given in Table II while lists of anisotropic thermal parameters and observed and calculated structure factors are available from the authors. Bond distances and angles are listed in Table III.

Discussion

[Cu(SA)$_2$(H$_2$O)$_2$] (1)

Complex (**1**) has square planar coordination about copper (Fig. 1). The centrosymmetric CuO_4 coordination sphere consists of two oxygens from *trans*-related unidentate phenoxy carboxylate groups [Cu–O, 1.933(2) Å] and two waters [Cu–Ow, 1.961-

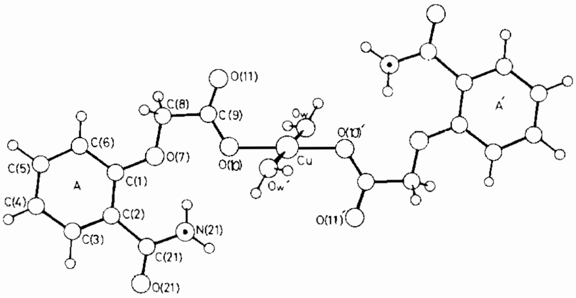

Fig. 1. Molecular configuration and atom numbering scheme for $[Cu(SA)_2(H_2O)_2]$ (1).

TABLE II. Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4)

	(1)				(2)			
	x/a	*y/b*	*z/c*	U_{eq}[a]	*x/a*	*y/b*	*z/c*	U_{eq}[a]
M	0	0	0	293(4)	0	0	0	221(3)
Ow(1)	2948(8)	830(3)	−738(2)	393(16)	65(2)	−2023(4)	906(1)	292(12)
Ow(2)	–	–	–	–	−1377(2)	−2691(4)	−513(1)	285(12)
C(1)	4051(9)	5580(3)	3182(3)	246(18)	−3532(3)	7862(6)	1411(2)	264(17)
C(2)	2336(9)	6409(3)	2561(3)	259(19)	−3256(3)	9328(6)	2028(1)	231(18)
C(3)	3434(10)	7882(4)	2993(3)	342(22)	−4147(3)	11216(7)	2106(2)	314(18)
C(4)	6123(11)	8513(4)	4011(4)	364(24)	−5274(3)	11601(7)	1610(2)	383(21)
C(5)	7749(10)	7682(4)	4626(3)	338(21)	−5547(3)	10068(7)	1014(2)	354(19)
C(6)	6722(9)	6216(4)	4211(3)	303(20)	−5321(3)	8208(7)	908(2)	321(20)
O(7)	2880(6)	4134(2)	2759(2)	270(13)	−2647(2)	6035(4)	1333(1)	328(12)
C(8)	5178(9)	3227(4)	3064(3)	278(19)	−2785(3)	4779(6)	685(1)	295(17)
C(9)	4104(10)	1832(4)	2138(3)	299(21)	−1655(2)	2958(6)	740(1)	235(16)
O(10)	1693(8)	1738(3)	1231(2)	321(15)	−1087(2)	2049(4)	1315(1)	283(11)
O(11)	5722(8)	913(2)	2353(2)	492(18)	−1427(2)	2423(4)	164(1)	261(11)
C(21)	−664(10)	5835(4)	1464(3)	303(20)	−2083(3)	9046(6)	2608(2)	286(17)
O(21)	−2243(7)	6662(3)	1043(2)	376(16)	−1993(3)	275(5)	3160(1)	395(13)
N(21)	−1609(9)	4453(3)	968(3)	321(18)	−1159(2)	7482(6)	2532(1)	387(17)
H(3)	1909	8503	2427		−3912	12307	2569	
H(4)	6060	9504	4389		−5954	13080	1687	
H(5)	10147	8260	5434		−6445	10333	6340	
H(6)	7957	5570	4590		−4805	7116	413	
H(81)	7723	3677	3143		−3468	3615	598	
H(82)	4825	3079	3803		−2837	6304	323	
HN(21)	−3192	3978	231		−346	7589	2897	
HN(22)	523	3972	1156		−1199	6247	2229	
Hw(11)	2539	1652	−948		−730	2094	−1120	
Hw(12)	3327	355	−1368		356	774	−1165	
Hw(21)	–	–	–		−1487	−3114	−989	
Hw(22)	–	–	–		1429	3890	335	

[a] U_{eq} is defined as $(U_{11} \times U_{22} \times U_{33})^{1/3}$.

(3) Å]. This mode of complexation is found also in diaquabis(4-methoxyphenoxyacetato)copper(II) dihydrate [Cu–O, 1.93, 1.96(2) Å] [9], diaquabis(2-carboxyphenoxyacetato)copper(II) [Cu–O, 1.91, 1.91(1) Å] [1] among the copper(II) phenoxyacetates and diaquabis(2-hydroxybenzoato)copper(II) [1.84, 1.92(2) Å] [10]. A second chemical polymorph of copper(II) 4-methoxyphenoxyacetate, a tetragonally distorted octahedral complex, diaquabis(4-methoxyphenoxyacetato)copper(II) [9] is also known, having the ether oxygens of the phenoxy ligands occupying the elongated axial sites of the coordination sphere. It is possible to perceive a transformation from polymorph (**1**) (square) to polymorph (**2**) (octahedral) by a simple rotation of the ligand, a process impeded by the steric crowding afforded by an *ortho*-substituent [as in complex (**1**)]. With one exception, the chelate mode has been found only for complexes of phenoxyalkanoic acids with either no ring substituent or with only a *para*-substituent (F, Cl, NO_2, OMe). However, this exception, the polymorph $[Cu(OCPA)(H_2O)]_n$ [1], differs from the other examples in that the *ortho*-substituent (COOH) is a coordinating group.

As in the other square planar phenoxy complexes, the phenoxyalkanoate ligand in (**1**) is approximately planar with this plane in turn perpendicular to the CuO_4 complex plane. Intraligand torsion angles are: C(2)–C(1)–O(7)–C(8), +155.6°, C(1)–O(7)–C(8)–C(9), −152.6°, O(7)–C(8)–C(9)–O(11), −173.9°, C(1)–C(2)–C(21)–N(21), −6.9°. The amide nitrogen is also directed towards the ether oxygen, with an intramolecular hydrogen bond between the two atoms (N···O, 2.63 Å) (Fig. 2). The nitrogen is also associated with the amide oxygen of an adjacent complex [2.90 Å], forming stacks down the *a* axis of the cell (4.08 Å). The uncoordinated carboxylate oxygen [O(11)] is similarly linked down *a* to coordinated waters in the same stack. Between the stacks, O(21) is associated with Ow (2.66 Å), providing a network which enhances complex stability in the crystal lattice.

TABLE III. Bond Distances (Å) and Angles (°)

(a) Coordination sphere		
(i) Distances		
(1)		
Cu–Ow(1)	1.961(3)	
Cu–O(10)	1.933(2)	
(2)		
Ni–Ow(1)	2.063(2)	
Ni–Ow(2)	2.076(2)	
Ni–O(11)	2.072(2)	
(ii) Angles		
(1)		
Ow(1)–Cu–O(10)	88.9(1)	
Cu–O(10)–C(9)	121.3(1)	
(2)		
Ow(1)–Ni–Ow(2)	88.2(1)	
Ow(1)–Ni–O(11)	89.8(1)	
Ow(2)–Ni–O(11)	88.7(1)	
Ni–O(11)–C(9)	127.3(1)	
(b) Intraligand		
(i) Distances		
	(1)	(2)
C(1)–C(2)	1.401(4)	1.399(4)
C(1)–C(6)	1.392(5)	1.396(4)
C(1)–O(7)	1.371(4)	1.370(4)
C(2)–C(3)	1.394(5)	1.396(5)
C(2)–C(21)	1.505(4)	1.491(4)
C(3)–C(4)	1.386(5)	1.377(5)
C(4)–C(5)	1.384(6)	1.383(5)
C(5)–C(6)	1.385(5)	1.386(5)
O(7)–C(8)	1.424(5)	1.414(3)
C(8)–C(9)	1.515(4)	1.517(4)
C(9)–O(10)	1.234(5)	1.241(3)
C(9)–O(11)	1.271(4)	1.272(4)
C(21)–O(21)	1.241(5)	1.247(4)
C(21)–N(21)	1.319(4)	1.320(4)
(ii) Angles		
	(1)	(2)
C(2)–C(1)–C(6)	120.7(3)	120.9(3)
C(2)–C(1)–O(7)	117.2(2)	117.2(2)
C(6)–C(1)–O(7)	122.0(3)	121.9(3)
C(1)–C(2)–C(3)	118.0(3)	117.5(2)
C(1)–C(2)–C(21)	125.1(3)	125.2(3)
C(3)–C(2)–C(21)	116.9(3)	117.3(3)
C(2)–C(21)–O(21)	119.8(3)	119.5(3)
C(2)–C(21)–N(21)	119.4(3)	119.7(3)
N(21)–C(21)–O(21)	120.8(5)	120.8(2)
C(2)–C(3)–C(4)	121.2(4)	122.2(3)
C(3)–C(4)–C(5)	120.2(5)	119.5(3)
C(4)–C(5)–C(6)	119.7(3)	120.3(3)
C(5)–C(6)–C(1)	120.2(4)	119.7(3)
C(1)–O(7)–C(8)	119.9(2)	119.7(2)
O(7)–C(8)–C(9)	109.8(3)	108.4(2)
C(8)–C(9)–O(10)	117.2(3)	118.9(3)
C(8)–C(9)–O(11)	115.5(3)	114.5(2)
O(10)–C(9)–O(11)	127.3(3)	126.5(3)

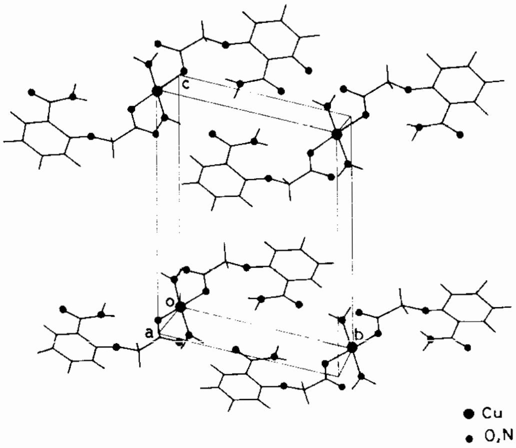

Fig. 2. Packing of (1) in the unit cell viewed perpendicular to *bc*.

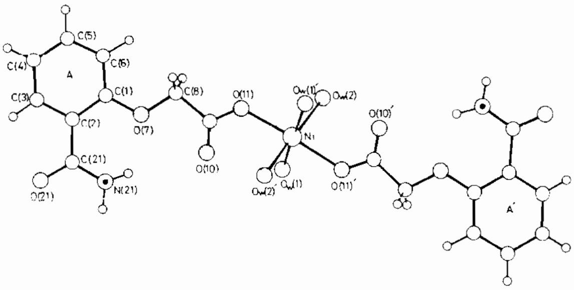

Fig. 3. Molecular configuration and atom numbering scheme for $[Ni(SA)_2(H_2O)_4]$ (2).

$[Ni(SA)_2(H_2O)_4]$ (2)

Complex (2) has regular centrosymmetric octahedral coordination about nickel (Fig. 3). The NiO_6 coordination polyhedron consists of two oxygens from *trans*-related unidentate carboxylate groups [Ni–O 2.072(2) Å] and four oxygens from coordinated water molecules [mean Ni–Ow, 2.069(2) Å]. Unlike the copper(II) complex (1), the coordinated carboxyl oxygen [O(10)] is the one derived from the 'carbonyl' rather than the 'hydroxyl' group. Retention of the synplanar-synplanar side-chain conformation for the 'carbonyl' oxygen is found, as is the case with the majority of the metal complexes of phenoxyacetic acids [11]. The side-chain conformation is confirmed on the basis of C–C–O(carboxyl) bond angles [C–C–O(carbonyl), 118.9(3)° > C–C–O-(hydroxyl), 114.5(2)°]. Distances and angles in the

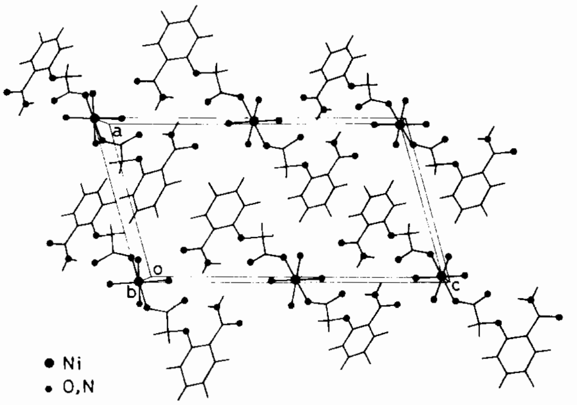

Fig. 4. Packing of (**2**) in the unit cell viewed perpendicular to *ac*.

coordination octahedron are considered normal while the structure compares with that of tetraaquabis(phenoxyacetato)nickel(II) [12]. The carbamoyl group is not involved in coordination with the metal but both the amide nitrogen [N(21)] and oxygen [O(21)] form hydrogen bonding interactions with adjacent complex units [N(21)···O(10)′, 2.90 Å; O(21)···Ow(1)′, 2.77 Å] (Fig. 4). Furthermore, discrete intramolecular O···O and O···N distances are found [uncoordinated carboxyl O(10)···Ow(1), 2.64 Å; O(10)···O(ether), 2.63 Å and O(ether)···N(21), 2.62 Å]. This results in a relatively planar conformation for the ligand, similar to that found in complex (**1**) and in the copper(II) complexes of 2-carboxyphenoxyacetatic acid [1]. Torsion angles for (2) are: C(2)–C(1)–O(7)–C(8), +165.3°; C(1)–O(7)–C(8)–C(9), −138.2°; O(7)–C(8)–C(9)–O(11), −157.3°; C(1)–C(2)–C(21)–N(21), +6.3°, comparable with those found for the ligand in complex (**1**).

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