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METAL-PHENOXYALKANOIC ACID INTERACTIONS—12†

THE CRYSTAL AND MOLECULAR STRUCTURE OF μ-AQUA-DI-μ-[(2-CHLOROPHENOXY)ETHANOATO-(*O, O'*)]-bis[(2-CHLOROPHENOXY)-ETHANOATO-BIS(PYRIDINE)NICKEL(II)]-WATER (1/1)

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Abstract—The crystal structure of the pyridine adduct of nickel (2-chlorophenoxy)-ethanote, $\{[Ni_2(2\text{-}CPA)_4(py)_4(H_2O)] \cdot H_2O\}$, has been determined from three dimensional X-ray data at 293 K. Crystals of the complex are triclinic, space group $P\bar{1}$, with two dimers in a unit cell of dimensions $a = 21.740(5)$, $b = 14.312(7)$, $c = 9.044(2)$Å, $\alpha = 96.69(4)$, $\beta = 84.99(4)$, $\gamma = 101.20(3)°$. The structure was solved by direct methods and refined to 0.059 for 2682 'observed' reflections. The dimer consists of two face-to-face NiO_4N_2 octahedra joined at their apical positions by a bridging water molecule [Ni(1)–Ow; 2.14(1)Å; Ni(2)–Ow, 2.10(1)Å; Ni(1)–Ôw–Ni(2), 116.9(4)°]. Two bidentate carboxyl groups of the 2–CPA molecules bridge the other two corners of the triangular face while the other two 2–CPA ligands are unidentate [Ni–O, 2.05(1)Å (mean)]. The coordination about each Ni is completed by two *cis*-related pyridine nitrogens [Ni–N; 2.11(1)Å (mean)]

Structural studies on the mode of interaction of univalent and divalent metal ions with the phenoxyalkanoic acids, which include the commercial auxin herbicides (2,4-dichlorophenoxy)ethanoic acid (2,4-D), (2,4,5-trichlorophenoxy)ethanoic acid (2,4,5-T) and (4-chloro-2-methylphenoxy)-ethanoic acid (MCPA), have shown a diversity of complex types.[1-3] Nickel(II) phenoxyalkanoates appear to be relatively stereotypical, as found in the only known X-ray examples, tetraaquabis-(phenoxyethanoato)nickel(II),[4] which has octahedral co-ordination with *trans*-related phenoxy ligands. However, reaction of an ethanolic solution of (2-chlorophenoxy)ethanoic acid (2-CPAH) with excess nickel(II) carbonate gave a pale green complex which appears (from elemental analysis, IR spectroscopy and DTA/TGA) to be atypical [empirical formula $Ni(2\text{-}CPA)_2(H_2O)_3$]. Poor crystallinity obviated a single crystal X-ray structure determination on this compound. In contrast, the pyridine adduct of this complex is a dark blue crystalline solid with empirical formula $Ni(2\text{-}CPA)_2(py)_2(H_2O)$. Since the IR spectrum and DTA/TGA did not resolve the anomaly of the sterochemistry for this formula, and preliminary X-ray photographs suggested the possibility of a dimeric structure (four formula units per triclinic cell), the X-ray structure determination was completed. The conformational aspects of the bonded 2-CPA ligands are also of interest since the structure of the parent acid (2-chlorophenoxy)ethanoic acid is known.[5]

EXPERIMENTAL

Preparation of $[Ni_2(2\text{-}CPA)_4(py)_4(H_2O)] \cdot H_2O$

The complex was prepared by treating an aqueous ethanolic solution of nickel(II) (2-chlorophenoxy)ethanoate, $[Ni(2\text{-}CPA)_2(H_2O)_3]$ (preparation, Ref. 1), with a dilute solution of pyridine in ethanol. The crystals grew from the solution as blue prisms after allowing some of the solvent to evaporate at room temperature. The compound was quite stable in air and in the X-ray beam even after 70 hr exposure. Analyses and structure work were completed on the air dried crystals without prior recrystallization. Elemental analyses (C, H,

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†Part 11.[1]

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Cl) were done by the University of Queensland Microanalytical Laboratory while Ni was determined titrimetrically using complexometric methods. IR spectra were determined on the samples as thin films in Nujol mulls using a Perkin–Elmer 598 spectrophotometer. A Rigaku instrument was used for thermogravimetric differential thermal analyses.

Analyses

(a) $[\mathrm{Ni(2\text{-}CPA)_2(H_2O)_3}]$. Found: C, 39.7; H, 3.96; Cl, 14.5% Calculated for $\mathrm{C_{16}H_{38}Cl_2Cu_2O_9}$: C, 39.7: H, 4.02; Cl, 14.1%.

(b) $[\mathrm{Ni(2\text{-}CPA)_4(py)_4(H_2O)}] \cdot \mathrm{H_2O}$. Found: C, 51.7; H, 4.04; Cl, 11.8; Ni, 9.87%. Calculated for $\mathrm{C_{52}H_{48}Cl_4N_4Ni_2O_{14}}$; C, 51.5; H, 3.95; Cl, 11.6; Ni, 9.69%.

Crystallography for $[\mathrm{Ni_2(2\text{-}CPA)_4(py)_4(H_2O)}] \cdot \mathrm{H_2O}$

Crystal data. $\mathrm{C_{52}H_{48}Cl_4N_4Ni_2O_{14}}$, $M = 1212.2$, triclinic, $a = 21.740(5)$, $b = 14.312(7)$, $c = 9.044(2)$Å, $\alpha = 96.69(4)$, $\beta = 84.99(4)$, $\gamma = 101.20(3)°$, $U = 2735$Å^3, $D_f = 1.48$, $D_c = 1.47\ \mathrm{g\,cm^{-3}}$, $Z = 2$, Mo-$K\alpha$ radiation, $\lambda = 0.7107$Å $\mu(\text{Mo-}K\alpha) = 9.52\ \mathrm{cm^{-1}}$, $F(000) = 1248$, space group $P\bar{1}$.

Data collection, structure solution and refinement

Three thousand nine hundred and eighty four reflections were collected from a single crystal (0.20 × 0.18 × 0.08 mm) mounted about the prism axis on an Enraf–Nonius CAD 4 automatic diffractometer ($2\theta_{\max} = 50°$; graphite monochromated Mo-$K\alpha$ radiation, $\lambda = 0.7107$Å). Of these, 2682 with $I > 2.5\sigma\ (I)$ 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[6] which provided the positions of the Ni atoms, while subsequent difference-Fourier syntheses gave all other heavy atoms. Blocked matrix least-squares refinement with only Ni and Cl atoms anisotropic reduced $R[= \Sigma \| Fo|\text{-}|Fc\| / \Sigma |Fo|]$ to 0.059 and $Rw\ [= (\Sigma w(\|Fo|\text{-}|Fc\|^2/\Sigma w|Fo|^2)^{\frac{1}{2}}]$ to 0.061, with $w = 1.68/(\sigma^2 Fo + 0.00076 Fo^2)$ found to be suitable. Some disorder was evident in the lattice water and in one of the pyridine rings. Allowance was made for the latter by including the atoms of this ring in the refinement with their site occupancy factors fixed at values determined from least-squares refinement. The maximim peak in the final difference-Fourier was 0.21 eÅ^{-3}. Neutral atom scattering factors were used.[7] Hydrogens were located in difference-Fourier syntheses and included in the refinement at fixed positions with their isotropic thermal parameters set invariant at 0.05Å^2.

Atomic coordinates, thermal parameters, observed and calculated structure factors and intraligand bond distances and angles have been deposited with the Editor as supplementary material; copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre. Bond distances and angles about the coordination polyhedron are given in Table 1.

DISCUSSION

The complex species in the title compound consist of two slightly distorted octahedra facially linked by two carboxylate *(O, O′)* bridges [Ni–O, 2.026(9)–2.066(9)Å; mean 2.040(9)Å] from two 2-CPA ligands, and an almost symmetrical bridge from a single aqua ligand [Ni(1)–Ow(1), 2.137(8)Å; Ni(2)–Ow(1), 2.097(8)Å, Ni(1)–$\hat{\mathrm{O}}$w(1)–Ni(2), 116.9(4)Å] (Fig. 1). The remaining three coordination positions about each Ni are occupied by a carboxyl oxygen of a unidentate 2-CPA ligand [Ni-O, 2.058(8), 2.080(9)Å] and two pyridine nitrogens [Ni–N, 2.102(14)–2.113(14)Å; mean, 2.108(14)Å]. The structure is stabilized by intramolecular hydrogen bonding involving the bridging water molecule [Ow(1)] and the uncomplexed oxygens of the carboxyl groups [O(10)a, 2.56Å and O(10)b, 2.65Å]. The lattice water Ow(2) is also associated with the carboxyl oxygen [O(10)] of one of these ligands [a] via a single hydrogen bond (2.83Å). No inter-dimer contacts less than 3Å, involving either lattice water, or carboxylate oxygens are found, indicating that the complex units are quite discrete in their packing mode (Fig. 2). Differential thermal/thermogravimetric analysis of the compound shows a two-step weight loss. The first, corresponding to the loss of a single water and two pyridines, takes place over the temperature range 80–120°C, while the second results in a further two-pyridine loss, occurring at 200°C. The low-temperature water loss represents the removal of the lattice water, the lability of which was indicated in the structure analysis. In contrast, the bridging water molecule, together with the 2-CPA ligands remain coordinated up to the decomposition point of the complex. A parallel analysis of $[\mathrm{Ni(2\text{-}CPA)_2(H_2O)_3}]$ showed a one-step loss of all three water molecules over the range 70–110°C, followed by progressive decomposition up to *ca.* 230°C. The IR spectrum for this compound indicates at least two different water environments, so it may be concluded that a water bridged system comparable to $[\mathrm{Ni_2(2\text{-}CPA)_4(py)_4(H_2O)}] \cdot \mathrm{H_2O}$ is not present. Al-

Table 1. Bond distances (Å) and angles (deg.) about the coordination sphere for $[Ni_2(2\text{–}CPA)_4(py)_2(H_2O)]\cdot H_2O$*

a. *Distances*

N(1)-N(1)ap	2.104(14)	Ni(2)-N(1)bp	2.112(15)
Ni(1)-N(1)cp	2.113(14)	Ni(2)-N(1)dp	2.106(13)
Ni(1)-O(11)a	2.058(8)	Ni(2)-O(11)b	2.080(9)
Ni(1)-O(11)c	2.026(9)	Ni(2)-O(10)c	2.037(8)
Ni(1)-O(11)d	2.031(9)	Ni(2)-O(10)d	2.066(9)
Ni(1)-Ow(1)	2.137(8)	Ni(2)-Ow(1)	2.097(8)

b. *Angles*

N(1)ap-Ni(1)-N(1)cp	91.3(5)	N(1)bp-Ni(2)-N(1)dp	90.6(5)
N(1)ap-Ni(1)-O(11)a	87.3(5)	N(1)bp-Ni(2)-O(11)b	91.9(5)
N(1)ap-Ni(1)-O(11)c	85.9(5)	N(1)bp-Ni(2)-O(10)c	87.3(5)
N(1)ap-Ni(1)-O(11)d	89.7(5)	N(1)bp-Ni(2)-O(10)d	177.3(5)
N(1)ap-Ni(1)-Ow(1)	174.7(4)	N(1)bp-Ni(2)-Ow(1)	90.9(4)
N(1)cp-Ni(1)-O(11)a	89.6(4)	N(1)dp-Ni(2)-O(11)b	88.0(4)
N(1)cp-Ni(1)-O(11)c	176.4(5)	N(1)dp-Ni(2)-O(10)c	89.3(4)
N(1)cp-Ni(1)-O(11)d	88.3(4)	N(1)dp-Ni(2)-O(10)d	86.7(4)
N(1)cp-Ni(1)-Ow(1)	93.5(4)	N(1)dp-Ni(2)-Ow(1)	177.6(4)
O(11)a-Ni(1)-O(11)c	87.9(3)	O(11)b-Ni(2)-O(10)c	177.2(3)
O(11)a-Ni(1)-O(11)d	176.3(3)	O(11)b-Ni(2)-O(10)d	88.3(3)
O(11)a-Ni(1)-Ow(1)	90.5(3)	O(11)b-Ni(2)-Ow(1)	90.1(3)
O(11)c-Ni(1)-O(11)d	93.9(3)	O(10)c-Ni(2)-O(10)d	92.4(3)
O(11)c-Ni(1)-Ow(1)	89.2(3)	O(10)c-Ni(2)-Ow(1)	92.6(3)
O(11)d-Ni(1)-Ow(1)	92.7(3)	O(10)d-Ni(2)-Ow(1)	91.8(3)
Ni(1)-Ow(1)-Ni(2)	116.9(4)		

* Intraligand bond distances and angles have been deposited with the Editor and are also available from the authors.

though carboxylate bridged Ni(II) dimers are known, e.g. in the acetate bridged $[Ni_2(phensal†)_4CH_3CO_2]^-$ complex,[8] a monoaqua bridge of the type found in the present example appears to be without precedence in the complex chemistry of nickel(II). The carboxylate *(O, O′)* bridges allow the two complex units to open out, increasing the Ni–Ni distance to 3.607(5)Å, which compares with 3.101(1)Å in the phensal complex and 3.161(3)Å in $[Ni_2(TFDAA‡)_2(py)_4]$,[9] where bis-oxo bridges are found in more symmetrical edge-shared octahedral dimers.

The four independent 2-CPA ligands show similar conformations in the dimer complex (Table 2). The parent acid (2-CPAH) is essentially planar,[5] the preferred conformation in the solid state of all phenoxyethanoic acids except those with both 2-*and* 6- substituents in the benzene ring. Furthermore, the free acids, without exception adopt the conformation of the side-chain with the "carbonyl" oxygen (rather than the "hydroxyl" oxygen) adjacent to and presumably interactive with the ether oxygen.[10] This O–O distance ranges from 2.605 to 2.775Å (mean, 2.771Å) for 19 examples of phenoxyalkanoic acids[10] (including propanoic acid analogues) and compares with 2.64(1)Å for the parent acid 2-CPAH. Also associated with this preferred conformation is a discrete angle difference between C–C–O (hydroxyl) and C–C–O (carbonyl) (usually < 120° and > 120° respectively), as is shown in 2-CPAH [mean for the two independant molecules in the asymmetric unit, 114.5(8) and 125.2(8)°]. It has also been found that the interactive O–O distance and the angle difference in the carboxyl group is usually retained with deprotonation, i.e. with complexation.[11] This does not depend on the type of metal involved or the nature of the mode of complexation (unidentate, bidentate, bridging). The C–O bond length

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†phensal = phenylsalicylaldimine.

‡TFDAA = 1,1,1-trifluoro-2,4,6-heptanetrionato.

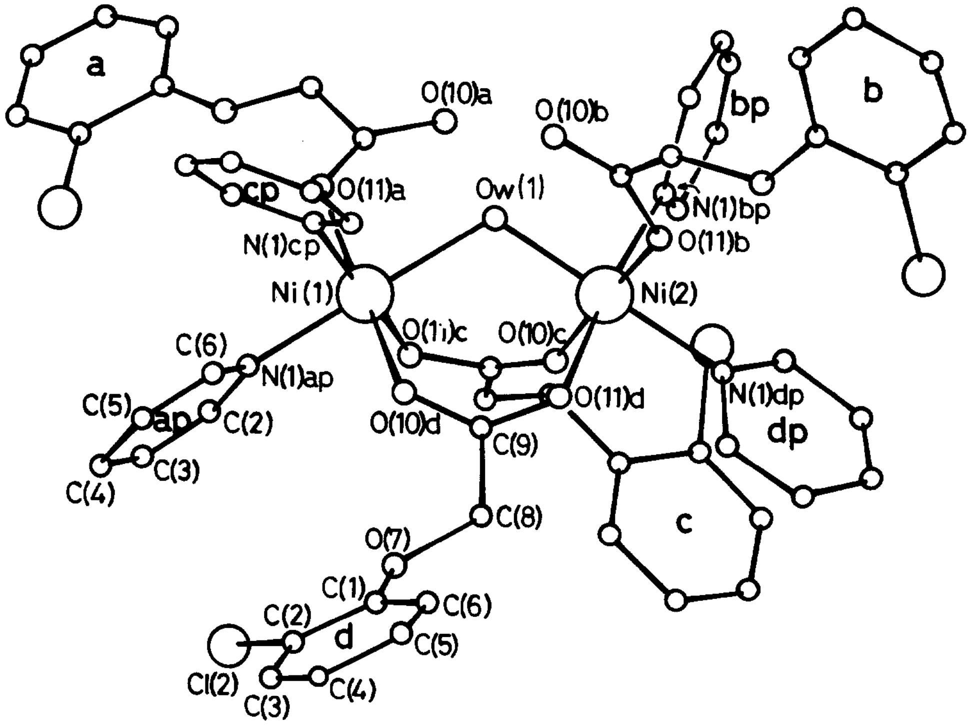

Fig. 1. Molecular configuration and atom naming scheme for $[Ni_2(2\text{–}CPA)_4(py)_4(H_2O)]$. Hydrogens are omitted for clarity.

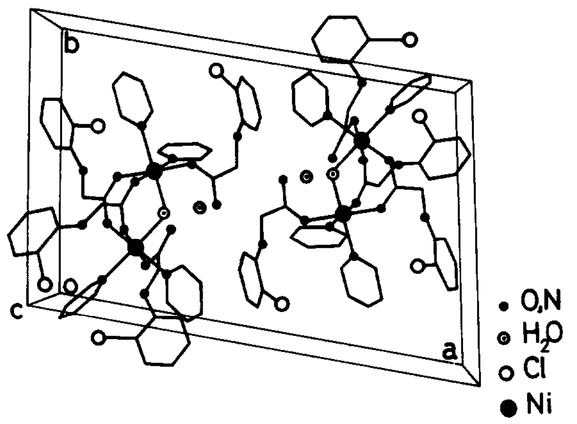

Fig. 2. Perspective view of the packing of the two molecular dimers in the unit cell viewed down the *c* axis.

difference is also a quantity which tends to be retained in proceeding from the acid to the anion, although it tends to be more susceptible to differences in the mode of complexation. It has generally been possible to determine the origin of the carboxyl oxygen as "carbonyl" or "hydroxyl" and hence ascertain if the side-chain conformation of the parent is retained or lost. In considering $[Ni_2(2\text{-CPA})_4(py)_2(H_2O]$, the classification is less definite than any previously considered examples,[1,2] possibly because of the lesser precision in this determination but assignments have been made on the basis of the following data.

For ligand (a), the conformation has changed [O(7)–O(11) (unidentate bonded), 2.69(1)Å; C(8)–C(9)–O(10), 116(2)°; C(8)–C(9)–O(11),

Table 2. Comparative torsion angles within the oxo-ethanoate ligands in $[Ni_2(2\text{–}CPA)_4(py)_4(H_2O)]\cdot H_2O$ and for the parent acid (2–CPAH)[5] (ESD's for angles are *ca.* 1°)

	a	b	c	d	2-CPAH*
C(2)-C(1)-O(7)-C(8)	-168	-166	-179	-177	-179, 180
C(1)-O(7)-C(8)-C(9)	+71	+68	+82	+72	-175, -173
O(7)-C(8)-C(9)-O(10)	+177	-165	+164	-162	-179, 180
O(7)-C(8)-C(9)-O(11)	-4	+15	-15	+21	-179, 180
C(8)-C(9)-O(11)-Ni(1)/(2)	+166	+170	+167	+166	-

* 2-CPAH has two crystallographically independent molecules in the asymmetric unit.

117(2)°; C(9)–O(11), 1.26(2)Å; C(9)–O(10), 1.22(2)Å]

For ligand (b), the conformation is retained. [O(7)–O(11) (bonded unidentate), 2.71(1)Å; C(8)–C(9)–O(11), 119(1)°; C(8)–C(9)–O(10), 114(1)°; C(9)–O(11), 1.24(2)Å; C(9)–O(10), 1.27(2)Å].

For ligand (c), the conformation has changed. [O(7)–O(11) (bridging), 2.75(1)Å; C(8)–C(9)–O(11), 112(1)°; C(8)–C(9)–O(10), 120(1)°; C(9)–O(11), 1.25(1)Å; C(9)–O(10), 1.25(1)Å].

For ligand (d), the conformation has probably changed. [O(7)–O(10) (bridging 2.66(1)Å; C(8)–C(9)–O(10), 114(1)°; C(8)—C(9)–O(11), 116(1)°; C(9)–O(10), 1.22(2)Å; C(9)–O(11), 1.24(2)Å].

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