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The Structure of Trinuclear Cu(II) Complex with Isonicotinic Acid N-Oxide, Pentaaquadi-μ-hydroxobis-μ-(ionicotinato N-oxide)bis(isonicotinato N-oxide)-tricopper(II) Dihydrate

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A new trinuclear Cu(II) complex with isonicotinic acid N-oxide, $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$, has been prepared and its crystal structure determined by X-ray analysis. The complex crystallizes in the monoclinic space group P2/c *with* a = *12.051(4),* b = *7.043(2),* c = *19.825(6)* Å, *β* = *98.51(2)° and* Z = *2.*

The arrangement of the three Cu atoms is triangular, with distances of 3.365(1) Å *between the central and terminal Cu atoms. The coppers are pentacoordinated; the coordination geometry is tetrahedral distorted square pyramidal for the terminal Cu atoms and elongated square pyramidal for the central Cu atom. Two hydroxo ligands and two of the four isonicotinato N-oxide ligands through the carboxyl group form bridges between Cu atoms. In addition to five coordinated waters, two lattice waters are present. The least-squares refinement led to a final* R *of 0.044.*

Introduction

Trinuclear Cu(II) complexes are formed by pyridine-2-carbaldehyde oxime [1] and amino-oxime ligand [2] with the μ_3-hydroxo-bridged, Schiff-base derivatives N,N′-ethylenebis(salicylaldimine) and N,N′-ethylenebis(O-hydroxoacetophenimine) [3], iminoalcohols [4] and nicotinic acid N-oxide [5]. Several oxygen-bridged trinuclear Cu(II) complexes formed by aminoalcohols have also been reported [6–11]. The arrangement of the Cu atoms is triangular in most of these complexes. Only a few crystal structures of linear trinuclear oxygen-bridged Cu(II) complexes are known: *e.g.* bis-[N,N′-di(3-hydroxopropyl)-2,4-pentanediimine]tricopper(II) [4], catena-diaquadi-μ-hydroxobis-μ-(nicotinato N-oxide)bis-μ(nicotinato N-oxido)tricopper(II) [5] and bis[μ-(benzoato-O,O′)]-bis(benzoato)-bis[μ-(2-dibutylaminoethanolato)]-bis(ethanol)tricopper(II) [11].

Nicotinic and isonicotinic acid N-oxides are able to form polynuclear Cu(II) complexes. The structures have been reported earlier for trinuclear Cu(II) complex with nicotinic acid N-oxide with hydroxo bridges [5] and of tetranuclear Cu(II) complex with isonicotinic acid N-oxide with μ-sulphato and μ_3-hydroxo bridges [12]. In the present paper we describe a triangular trinuclear Cu(II) complex with isonicotinic acid N-oxide.

In compounds of known structure the isonicotinate N-oxide group coordinates to the central metal atom through one carboxylato oxygen atom, as in tetraaquabis(isonicotinato N-oxide)Mn(II) [13] and diaquabis(isonicotinato N-oxide)-bis(pyridine)Cu(II) [14], or through both carboxylato oxygen atoms, either chelating as in diaquabis(isonicotinato N-oxide)Cu(II) [14] or bridging as in tetranuclear Cu(II) complex [12]. Isonicotinic acid N-oxide forms with Fe(II) [13], Co(II) and Ni(II) ions [15] ionic compounds containing the hexaaquametal(II) cation.

Experimental

Preparation of the Complex

Bright green crystals were prepared by the method used earlier [12] modified from the procedure employed in preparing metal complexes of pyridine monocarboxylic acid N-oxides [16, 17].

Hydrated copper(II) nitrate and isonicotinic acid N-oxide (N-inicOH) were the starting materials. Ammonium isonicotinate N-oxide was prepared as an intermediate.

Two kinds of crystals, $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$ and $[Cu(N\text{-}inicO)_2(H_2O)_2]$, were precipitated from a reaction solution to which solid

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TABLE I. Crystal and Refinement Data of $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$.

M	903.17	Collection	$\theta/2\theta$
Space group	$P2/c$	Radiation	MoKα
a (Å)	12.051(4)	Scan range	$4° < 2\theta < 55°$
b	7.043(2)	Scan rate (° min^{-1})	1.0 to 20.0
c	19.825(6)	Refl. meas.	2962
β (°)	98.51(2)	obs. ($I > 3\sigma(I)$)	1962
Z	2	F(000)	918
V ($Å^3$)	1664.1	Residual electron	
D_o ($g\ cm^{-3}$)	1.76	density ($eÅ^{-3}$)	0.69
D_c ($g\ cm^{-3}$)	1.80	R ($= \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$)	0.044

sodium acetate and/or ethanol had been added. The structure of $[Cu(N\text{-}inicO)_2(H_2O)_2]$ has been determined earlier [14].

Physical Methods

Copper was analyzed by a Perkin-Elmer ICP/5000 inductively coupled plasma. The chemical analysis for C, N and H was performed by the Pulp and Paper Research Institute, Espoo, Finland. *Anal.* Calcd for $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$: Cu 21.11%, C 31.92%, N 6.20%, H 3.57%. Found: Cu 21.65%, C 31.59%, N 6.22%, H 3.57%.

The i.r. spectrum was run from the sample in a KBr disc on a Perkin-Elmer 283 infrared spectrophotometer in the range 4000–200 cm^{-1}.

Data Collection

The crystal and refinement data are given in Table I. The preliminary unit cell was determined from Weissenberg photographs. The crystal and intensity data were measured on a Syntex $P2_1$, four-circle diffractometer using graphite monochromatized MoKα radiation. The final unit cell parameters were calculated by least squares refinement of 15 high order reflections. The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 20.7\ cm^{-1}$).

Structure Determination

The structure was solved by direct methods [18] and Fourier techniques and refined by block diagonal matrix least squares with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms except two were located by difference Fourier syntheses. The positions of these two were calculated geometrically assuming the C–H bond to be 1.00 Å and refined isotropically. The final R-value was 0.044.

All calculations were carried out with X-Ray System Programs [19] on a UNIVAC 1100/60 computer. The anomalous dispersion corrections for copper atoms were included in calculations. The scattering factors for Cu, C, N and O were those of Cromer and Mann [20] and for hydrogen atoms those reported by Stewart *et al.* [21].

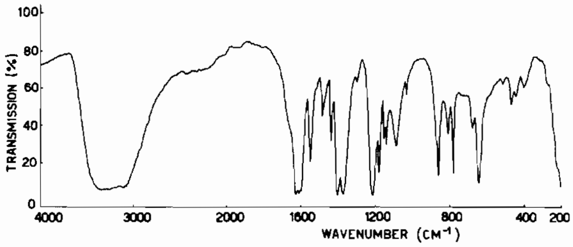

Fig. 1. The infrared spectrum of $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$.

The final atomic coordinates and anisotropic temperature factors for nonhydrogen atoms are given in Table II and the coordinates and isotropic temperature factors for hydrogen atoms in Table III.

Results and Discussion

Infrared Spectrum

Figure 1 shows the IR spectrum for $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$.

The coordinated aqua ligands and free lattice waters give a very strong broad $\nu(OH)$ absorption in the region 3100–3400 cm^{-1}. The H–O–H bending motion occurs with asymmetric stretching vibrations of carboxylato groups in the same region near 1600 cm^{-1}. The broad absorption has been divided into three peaks, 1626, 1613 and 1603 cm^{-1}. The carboxylato groups show symmetric stretching absorption bands at 1405 and 1373 cm^{-1}. The N–O stretching absorption is at 1217 cm^{-1} and the N–O bending motion at 861 cm^{-1}.

TABLE II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters ($\times 10^2$) for Non-hydrogen Atoms, with Their Standard Deviations. The anisotropic parameters are of the form $\exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}))$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.5000	0.1980(1)	0.7500	4.57(6)	3.47(3)	1.22(2)	–	0.29(3)	–
Cu(2)	0.2452(1)	0.2813(1)	0.6603(1)	4.96(5)	3.52(2)	1.19(1)	0.28(3)	0.34(2)	0.04(2)
O(1)	0.8912(3)	0.2472(4)	0.4472(1)	5.6(3)	4.3(1)	1.7(1)	0.4(2)	1.5(1)	–0.0(1)
O(2)	0.3907(2)	0.8242(4)	0.3149(1)	1.8(2)	7.5(2)	2.2(1)	–0.1(2)	0.6(1)	–1.0(1)
O(3)	0.7691(3)	0.7070(4)	0.2417(1)	8.9(3)	4.4(1)	1.5(1)	0.4(2)	0.4(1)	0.1(1)
O(4)	0.1688(3)	0.2419(3)	0.2437(1)	10.8(3)	3.7(1)	1.3(1)	–0.2(2)	0.3(1)	–0.1(1)
O(5)	0.7712(3)	0.7096(4)	0.4392(1)	5.6(3)	6.7(2)	1.6(1)	1.3(2)	0.8(1)	0.1(1)
O(6)	0.4097(3)	0.7321(6)	0.0448(1)	3.3(3)	16.3(4)	2.6(1)	0.1(3)	1.0(1)	–1.7(2)
O(7)	0.6117(2)	0.8403(4)	0.3267(1)	2.7(2)	4.3(1)	1.9(1)	0.6(1)	0.1(1)	0.2(1)
O(8)	0.5000	0.4811(6)	0.2500	7.3(4)	4.1(2)	5.3(2)	–	–0.0(2)	–
O(9)	0.1285(3)	0.5171(3)	0.1509(1)	6.4(3)	3.1(1)	2.1(1)	–0.9(1)	0.6(1)	–0.2(1)
O(10)	0.8787(3)	0.9591(3)	0.3498(1)	5.7(3)	3.3(1)	2.7(1)	–0.1(2)	0.4(1)	0.1(1)
O(11)	0.3704(3)	0.2285(4)	0.1664(1)	8.0(3)	4.9(2)	4.2(1)	–0.6(2)	0.3(2)	–0.3(1)
N(1)	0.1538(3)	0.2455(4)	–0.0049(1)	5.6(3)	3.0(2)	1.7(1)	–0.3(2)	0.7(1)	–0.0(1)
N(2)	0.2017(3)	0.2522(4)	0.3112(1)	7.4(3)	2.5(2)	2.0(1)	0.2(2)	1.3(2)	0.1(1)
C(1)	0.2648(4)	0.7685(6)	0.4977(2)	5.6(4)	4.7(2)	1.8(1)	0.7(2)	0.1(2)	0.1(2)
C(2)	0.3137(4)	0.7726(6)	0.4379(2)	3.5(4)	4.5(2)	2.1(1)	0.5(2)	0.5(2)	–0.1(1)
C(3)	0.7594(4)	0.7605(5)	0.1243(1)	5.5(4)	2.6(2)	1.5(1)	–0.6(2)	0.8(2)	0.2(1)
C(4)	0.8721(4)	0.7437(5)	0.1249(2)	2.6(4)	4.2(2)	2.6(1)	0.0(2)	0.6(2)	–0.1(1)
C(5)	0.0847(4)	0.7433(5)	0.4355(2)	3.4(4)	4.0(2)	2.3(1)	–0.1(2)	0.7(2)	0.1(1)
C(6)	0.7051(4)	0.2338(5)	0.6899(1)	4.0(4)	3.6(2)	1.3(1)	1.1(2)	–0.5(2)	0.3(1)
C(7)	0.8791(4)	0.2457(6)	0.1481(2)	4.7(4)	4.4(2)	3.1(2)	–0.1(2)	0.8(2)	–0.1(2)
C(8)	0.8455(4)	0.2561(6)	0.0780(2)	2.1(4)	4.8(2)	2.6(2)	–0.1(2)	0.3(2)	0.4(2)
C(9)	0.2659(4)	0.2701(5)	0.4481(1)	4.0(4)	3.3(2)	2.1(1)	0.1(2)	1.6(2)	0.2(1)
C(10)	0.3486(4)	0.2769(7)	0.4044(2)	6.0(4)	6.4(3)	2.5(2)	–0.2(3)	1.6(2)	0.4(2)
C(11)	0.6891(4)	0.2688(7)	0.1651(2)	4.7(4)	6.4(3)	3.0(2)	0.1(3)	1.7(2)	–0.2(2)
C(12)	0.6908(4)	0.7229(6)	0.4748(2)	4.7(4)	4.8(2)	2.3(1)	0.2(3)	0.4(2)	0.4(2)

TABLE III. Final Positional Parameters and Isotropic Thermal Parameters ($\times 10^2$) for Hydrogen Atoms with Their Standard Deviations.

	x	y	z	U
H(1)	0.322(3)	0.233(5)	0.045(1)	2(1)
H(2)	0.409(4)	0.776(6)	0.444(2)	7(2)
H(3)	0.912(3)	0.732(4)	0.172(1)	2(1)
H(4)	–0.006(3)	0.716(5)	0.434(2)	5(2)
H(5)	0.023(4)	0.240(8)	0.320(2)	11(2)
H(6)	0.914(3)	0.248(5)	0.050(2)	5(2)
H(7)	0.419(6)	0.299(12)	0.420(4)	20(3)
H(8)	0.616(4)	0.252(6)	0.197(2)	6(2)
H(9)	0.575(3)	0.793(6)	0.361(2)	5(2)
H(10)	0.546(4)	0.393(7)	0.286(2)	10(2)
H(11)	0.120(4)	0.438(6)	0.114(2)	6(2)
H(12)	0.864(4)	0.452(6)	0.315(2)	7(2)
H(13)	0.870(4)	0.017(7)	0.309(2)	9(2)
H(14)	0.110(4)	0.038(7)	0.114(2)	8(2)
H(15)	0.325(4)	0.252(7)	0.181(2)	8(2)
H(16)	0.398(5)	0.115(9)	0.168(3)	15(2)

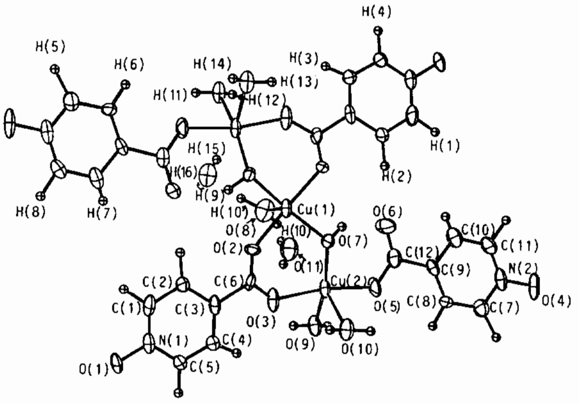

Fig. 2. The atomic labelling and the molecule of $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$ in the *ac* plane.

Description and Discussion of the Structure

The structure of $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$ consists of three pentacoordinated copper(II) ions, four isonicotinato N-oxide groups of which two

TABLE IV. Selected Interatomic Distances (Å) and Angles (°) with Their Standard Deviations.

Environment of copper(II) ions					
Cu(1)–O(2)	1.979(3)	O(2)–Cu(1)–O(7)	85.97(11)	O(7)–Cu(1)–O(8)	98.19(8)
Cu(1)–O(7)	1.895(2)	O(2)–Cu(1)–O(8)	94.53(9)	O(7)–Cu(1)–O(2)	92.74(11)
Cu(1)–O(8)	2.260(4)	O(2)–Cu(1)–O(2)	170.94(13)	O(7)–Cu(1)–O(7)	163.62(11)
Cu(2)–O(3)	1.978(2)	O(3)–Cu(2)–O(5)	168.52(14)	O(5)–Cu(2)–O(10)	88.16(11)
Cu(2)–O(5)	1.954(2)	O(3)–Cu(2)–O(7)	95.39(11)	O(5)–Cu(2)–O(9)	85.24(11)
Cu(2)–O(7)	1.909(3)	O(3)–Cu(2)–O(10)	88.07(11)	O(7)–Cu(2)–O(10)	104.41(11)
Cu(2)–O(9)	1.987(3)	O(3)–Cu(2)–O(9)	84.26(11)	O(7)–Cu(2)–O(9)	161.05(11)
Cu(2)–O(10)	2.247(3)	O(5)–Cu(2)–O(7)	96.05(11)	O(10)–Cu(2)–O(9)	94.52(11)
Pyridine N-oxido group					
O(1)–N(1)	1.337(4)	O(1)–N(1)–C(1)	119.9(3)		
N(1)–C(1)	1.334(6)	O(1)–N(1)–C(5)	118.4(3)		
N(1)–C(5)	1.343(4)	C(1)–N(1)–C(5)	121.7(3)		
C(1)–C(2)	1.399(5)	C(2)–C(1)–N(1)	121.0(3)		
C(2)–C(3)	1.409(4)	C(1)–C(2)–C(3)	117.0(4)		
C(3)–C(4)	1.362(6)	C(4)–C(3)–C(2)	120.4(3)		
C(4)–C(5)	1.375(5)	C(3)–C(4)–C(5)	119.9(3)		
		C(4)–C(5)–N(1)	120.0(4)		
O(4)–N(2)	1.343(3)	O(4)–N(2)–C(7)	116.4(3)		
N(2)–C(7)	1.355(6)	O(4)–N(2)–C(11)	120.1(3)		
N(2)–C(11)	1.335(6)	C(7)–N(2)–C(11)	123.5(3)		
C(7)–C(8)	1.391(4)	C(8)–C(7)–N(2)	117.7(4)		
C(8)–C(9)	1.368(6)	C(7)–C(8)–C(9)	120.4(4)		
C(9)–C(10)	1.415(6)	C(10)–C(9)–C(8)	120.8(3)		
C(10)–C(11)	1.387(5)	C(9)–C(10)–C(11)	116.7(4)		
		N(2)–C(11)–C(10)	120.9(4)		
Carboxylato group					
C(6)–C(3)	1.540(5)	O(2)–C(6)–O(3)	129.4(3)		
C(6)–O(2)	1.215(5)	O(2)–C(6)–C(3)	117.4(3)		
C(6)–O(3)	1.259(4)	O(3)–C(6)–C(3)	113.2(4)		
C(12)–C(9)	1.542(4)	O(5)–C(12)–O(6)	128.7(3)		
C(12)–O(5)	1.284(5)	O(5)–C(12)–C(9)	112.1(4)		
C(12)–O(6)	1.218(6)	C(9)–C(12)–O(6)	119.3(4)		

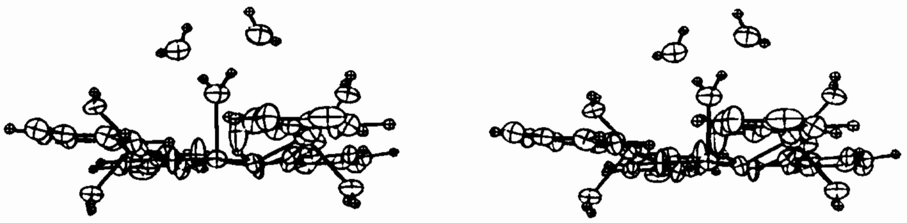

Fig. 3. A stereoview of the molecule in the *ab* plane.

are bridged ligands, two μ-hydroxo groups, five water molecules are coordinated to the copper atoms and two water molecules are present as lattice water. The labelling and structure of the molecule are shown in Fig. 2. Stereoviews of the molecule and the packing in the unit cell can be seen in Figs. 3 and 4 respectively. Interatomic distances and angles with estimated standard deviations in parentheses are given in Table IV.

TABLE V. Deviations (Å) of Atoms from Least-squares Planes.

Plane 1:	O(5), O(3), O(7), O(9) O(5) 0.184, O(3) 0.184, O(7) –0.169, O(9) –0.199, Cu(2) 0.136
Plane 2:	Cu(1), O(2), C(6), O(3), Cu(2), O(7) Cu(1) –0.275, O(2) –0.312, C(6) 0.077, O(3) 0.385, Cu(2) 0.507, O(7) –0.382
Plane 3:	O(2), O(7), O(2′), O(7′) O(2) 0.057, O(7) –0.057, O(7′) –0.057, O(2′) 0.057, Cu(1) 0.213

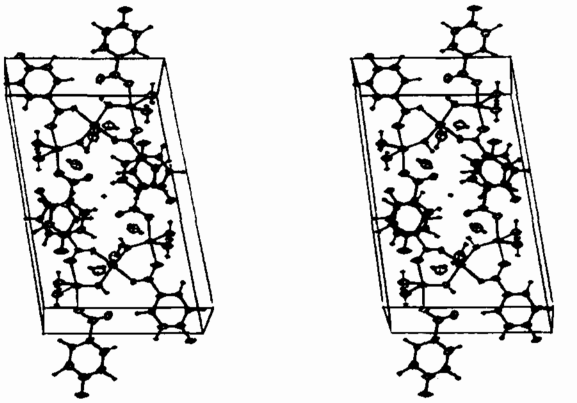

Fig. 4. A stereoview of the packing of the molecules in the unit cell.

The molecule of $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_5]\cdot 2H_2O$ is symmetric with the Cu(1) atom and the oxygen atom O(8) of the aqua ligand joined to Cu(1). These atoms lie on the two fold rotation axis, occupying the special positions (½, 0.1980, ¾) and (½, 0.4811, ¾) respectively.

The coordination geometry of Cu(1) is elongated square pyramidal. The Cu(1) atom is 0.213 Å above the plane of the basal oxygen atoms O(2), O(7), O(2′) and O(7′) (Table V). The Cu(2) and Cu(2′) atoms are symmetrically joined to the Cu(1) atom via a μ-hydroxo bridge and an isonicotinato N-oxide bridge through both carboxylato oxygen atoms. The deviations of the atoms Cu(1), O(2), C(6), O(3), Cu(2) and O(7) of the formed 6-membered ring from the least-squares plane are listed in Table V. The Cu(1)–Cu(2) distance is 3.365(1) Å.

The coordination geometry of the Cu(2) and Cu(2′) atoms is elongated square pyramidal with tetrahedrally distorted basal oxygen atoms O(3), O(7), O(5) and O(9) (Table V). The Cu(2) (Cu(2′)) atom lies 0.136 Å above the basal plane. In addition to the bridging groups one isonicotinato N-oxide group has coordinated monodentately through one carboxylato oxygen atom to the Cu(2) (Cu(2′)) atom. One of the two aqua ligands joined to the Cu(2) atom is in the apical position and its Cu–O distance, 2.247(3) Å, is longer than the basal Cu–O distances (1.909(3)–1.987(3) Å). The Cu–O-(hydroxo) distance is the shortest. The Cu–O(μ-hydroxo) bond distances, 1.909(3) and 1.985(2) Å, are in agreement with the Cu–O(μ-hydroxo) distances in trinuclear copper(II) complexes [4, 5].

Nicotinic acid N-oxide forms with Cu(II) a polynuclear complex [5] crystallizing in the space group P$\bar{1}$: catenadiaquadi-μ-hydroxobis-μ-(nicotinato N-oxide)bis-μ-(nicotinato N-oxide)tricopper(II), $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_2]_n$, whose structure is very similar to the title compound. By contrast, the Cu(II) complex with nicotinato N-oxide is polymeric with polymerization proceeding through the N-oxide groups. The arrangement of the three copper atoms is linear in the nicotinato N-oxide complex and triangular in the isonicotinato N-oxide complex. The central copper atom is tetracoordinated in $[Cu_3(N\text{-}inicO)_4(OH)_2(H_2O)_2]_n$, the geometry of coordination being square planar. In addition to the coordinated aqua ligands, lattice waters are present in the present Cu(II) complex with isonicotinic acid N-oxide.

Bond distances in these complexes conform with each other quite well. The distances for carboxyl and N-oxide substituents in the meta-position of nicotinato N-oxide groups and the para-position of isonicotinato N-oxide groups display some differences, however. The N–O bond lengths for isonicotinato N-oxide are longer than those for nicotinato N-oxide: 1.337(4), 1.343(3) Å and 1.327(3), 1.322(2) Å, respectively. In the same way the C–C bond lengths of the carboxyl group are longer: 1.540(5), 1.542(4) Å and 1.504(3), 1.503(3) Å, respectively. The C–O bond lengths in the bridged carboxylato groups are 1.215(5) and 1.259(4) for isonicotinato N-oxide and 1.240(2) and 1.250(3) Å for nicotinato N-oxide. In the monodentate carboxylato group, C–O bonds are longer for the isonicotinato N-oxide (1.284(5), 1.218(6) Å *vs.* 1.262(2), 1.208(2) Å).

In the crystal lattice of the title compound the molecules are joined to each other by hydrogen

TABLE VI. Hydrogen Bonds (Å).

A–H···B	A–H	H···B	A–B	<AHB (°)
O(8)–H(10)···O(11)	1.04(5)	1.72(5)	2.754(4)	170(4)
O(9)–H(11)···O(1)	0.91(4)	1.80(4)	2.703(3)	170(4)
O(9)–H(12)···O(4)	0.81(4)	1.88(4)	2.666(3)	161(4)
O(10)–H(14)···O(1)	0.90(4)	1.91(4)	2.789(3)	165(4)
O(10)–H(13)···O(4)	0.89(4)	1.92(5)	2.722(3)	149(4)
O(7)–H(9)···O(6)	0.92(4)	1.91(4)	2.709(3)	144(3)

bonds (Table VI). The lattice waters are connected by hydrogen bonds to the aqua ligand coordinated to the central copper atom (Cu1). The aqua ligands coordinated to the terminal copper atoms Cu(2), Cu(2′) form intermolecular hydrogen bonds to the oxygen atoms of N-oxide groups. Intramolecular hydrogen bonds are present between μ-hydroxo ligands and the monodentate carboxo group coordinated to the terminal copper atoms, at which a 6-membered ring forms.

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