

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 16

**X-RAY STRUCTURAL STUDIES ON SOME Cu (II), Co (II)
AND Ni (II) COMPLEXES WITH NICOTINIC AND
ISONICOTINIC ACID N-OXIDES**

**BY
HILKKA KNUUTTILA**

Academic Dissertation
for the Degree of
Doctor of Philosophy



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Knuuttila, H. and Knuuttila, P. The Crystal and Molecular Structures of Two Isonicotinato N-oxide Complexes of Cu(II), *Acta Chem. Scand. Ser. A* **37** (1983) 227-233.

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to my mother and mother-in-law

PREFACE

The experimental work of this study was carried out at the Department of Chemistry, University of Jyväskylä, during the years 1979-1982.

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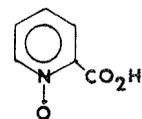
Jyväskylä, May 1983

Hilkka Knuutila

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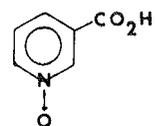
ABBREVIATIONS

N-picOH 2-pyridinecarboxylic acid 1-oxide,
picolinic acid N-oxide



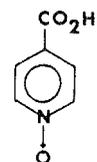
N-picO picolinate N-oxide,
picolinato N-oxide

N-nicOH 3-pyridinecarboxylic acid 1-oxide,
nicotinic acid N-oxide



N-nicO nicotinate N-oxide,
nicotinato N-oxide

N-inicOH 4-pyridinecarboxylic acid 1-oxide,
isonicotinic acid N-oxide



N-inicO isonicotinate N-oxide,
isonicotinato N-oxide

py pyridine

ABSTRACT

Five new copper(II) complexes with nicotinic and isonicotinic acid N-oxides have been synthesized and their crystal and molecular structures determined by single crystal X-ray diffraction measurements.

Catena-diaqua-di- μ -hydroxo-bis- μ -(nicotinato N-oxide)bis- μ -(nicotinato N-oxido)tricopper(II), $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$, is a polymeric complex with nicotinato N-oxide bridges between trinuclear structural units. Copper atoms are connected by hydroxo, N-oxide oxygen and carboxylato bridges.

Catena-diaqua-bis- μ -(nicotinato N-oxido)copper(II) tetrahydrate, $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, is an unstable polymeric complex. The decomposition has been studied thermogravimetrically.

Dichlorobis(nicotinic acid N-oxide)copper(II), $[\text{CuCl}_2(\text{N-nicOH})_2]$ was prepared in ethanol solution. The nicotinic acid N-oxide ligand is coordinated to the copper atom through the N-oxide oxygen atom.

Diaquabis(isonicotinato N-oxide)bis(pyridine)-copper(II), $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$, a complex unstable in air, was prepared through recrystallization of diaquabis(isonicotinato N-oxide)copper(II) in ethanol - pyridine solution.

Pentaaqua-di- μ -hydroxo-bis- μ -(isonicotinato N-oxide)-bis(isonicotinato N-oxide)tricopper(II) dihydrate, $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$, is a trinuclear complex with

hydroxo and carboxylato bridges between copper atoms.

Crystal and molecular structures were also determined for diaquabis(isonicotinato N-oxide)copper(II), $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ and for the isomorphous complexes tetraaquabis(nicotinato N-oxide)cobalt(II), $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$, and tetraaquabis(nicotinato N-oxide)nickel(II), $[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$.

The results are summarized and discussed.

1. INTRODUCTION

Octahedral, square-pyramidal, trigonal-bipyramidal, tetrahedral and square-planar coordination geometries predominate among the stereochemistries of the complexes of first-row transition metals.

The coordination numbers four, five and six are typical for the copper(II) ion. The copper(II) ion is reluctant to take up regular (octahedral and tetrahedral) stereochemistries, however, and characteristically prefers distorted forms of the basic stereochemistries because the $3d^9$ outer electron configuration lacks cubic symmetry. The variations in the arrangements occur through bond distance and bond angle distortion.

Pyridine monocarboxylic acid N-oxides have two groups, the carboxylic and N-oxide groups in ortho-, meta- or para-position, competing for the coordination sites of a metal ion. The carboxylate group can exist in ionic form in a crystal lattice or coordinate monodentately or bidentately, chelating or bridging, or both, in several ways. The characteristic coordination modes of the carboxylate group yield mono-, di- and polynuclear structures. For its part the N-oxide oxygen can coordinate monodentately or act as a bridge between metal ions. There are thus numerous possibilities for the complexes.

Many metal complexes of pyridine monocarboxylic acid N-oxides have been synthesized and characterized and their kinetic, magnetic and spectral properties have been

studied.⁷⁻²⁰ All known structures of the metal complexes of picolinic acid N-oxide contain six-membered chelate rings formed through the N-oxide and one carboxylato oxygen atom.²¹ Isonicotinic acid N-oxide forms an ionic compound with Fe(II), Co(II) and Ni(II) ions^{22,23} and coordinates to the Mn(II) ion monodentately through the carboxylato oxygen atom.²² In tetranuclear Cu(II) complex isonicotinato N-oxide acts as a bidentate ligand coordinating through both carboxylato oxygen atoms.²⁴

The present investigation continues the study on the structures of metal complexes with pyridine monocarboxylic acid N-oxides in this laboratory. The interest was specially directed to preparing new Cu(II) complexes of nicotinic and isonicotinic acid N-oxides and determining their structures, to learn more about the coordination mode of pyridine monocarboxylic acid N-oxides.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Compounds

Four Cu(II) and the Co(II) and Ni(II) complexes were prepared from aqueous solution by modifying the general procedure used to prepare metal complexes of pyridine monocarboxylic acid N-oxides. ^{8,13,16} Ammonium nicotinate N-oxide or ammonium isonicotinate N-oxide prepared as an intermediate was allowed to react with the appropriate hydrated metal sulfate, except in the case of $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ where copper(II) nitrate was used. The ligand:metal mole ratio was 2:1 or 1:1.

Polymeric $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ crystallize from the same reaction solution, the former from hot solution and the latter at room temperature. $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ can also be precipitated as the only product from the cooled reaction solution.

Trinuclear $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ was precipitated with $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ when solid sodium acetate and/or ethanol was added to the reaction solution.

Two Cu(II) complexes were prepared from organic medium. Recrystallization of $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ from ethanolic pyridine solution yielded $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$. $[\text{CuCl}_2(\text{N-nicOH})_2]$ was crystallized from ethanol solution of copper(II) chloride hydrate and nicotinic acid N-oxide with a few drops of 2 M HCl.

$[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ readily releases its lattice waters and $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ decomposes by loss of pyridine in air. $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ decomposes slowly during storage.

The details of the preparation of the complexes are given in papers 1 - 6.

2.2. Thermal Measurements

Thermogravimetric curves were run in static air on a Fisher 100 TG system. The sample weight was about 10 mg and heating rate $2.5^\circ\text{C}/\text{min}$.

2.3. X-Ray Data Collection

Crystal and intensity data were measured on a Syntex P2₁ automatic four-circle diffractometer, employing graphite monochromatized $\text{MoK}\alpha$ -radiation ($\lambda=0.71069 \text{ \AA}$) for data collection. The preliminary unit cell dimensions for $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ were estimated from rotation and Weissenberg photographs. Ni-filtered $\text{CuK}\alpha$ -radiation ($\lambda=1.5418 \text{ \AA}$) was then used. The final unit cell parameters were calculated by least-squares refinement of 15 high order reflections. The crystal and refinement data for the complexes are given in Table 1.

Table 1. Crystal data and some refinement data for the complexes.

Complex	a (Å)	b (Å)	c (Å)	α ($^{\circ}$)	β ($^{\circ}$)	γ ($^{\circ}$)	Ref.
$[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$	7.881(9)	9.658(11)	10.368(12)	97.32(9)	110.38(9)	109.53(9)	1
$[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	4.84(1)	27.55(7)	6.77(1)	90.0	106.08(17)	90.0	2
$[\text{CuCl}_2(\text{N-nicOH})_2]$	6.019(4)	13.155(11)	10.418(8)	90.0	115.80(5)	90.0	3
$[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$	14.136(7)	9.791(3)	10.768(3)	90.0	110.91(3)	90.0	4
$[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$	7.036(5)	9.540(3)	9.752(4)	110.05(3)	70.95(5)	104.28(5)	4
$[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	12.051(4)	7.043(2)	19.825(6)	90.0	98.51(2)	90.0	5
$[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$	8.896(5)	13.363(9)	6.719(3)	90.0	109.40(4)	90.0	6
$[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$	8.852(9)	13.277(16)	6.657(5)	90.0	108.79(7)	90.0	6

Table 1. continued

V (Å ³)	Formula	F.W.	D _c (Mgm ⁻³)	Z	F(300)	Space group	μMoKα (cm ⁻¹)	Reflections		R ^a	Ref.
								measd.	obs. I>3σ(I)		
670(1)	C ₂₄ H ₂₂ Cu ₃ N ₄ O ₁₆	813.09	2.01	1	439	P $\bar{1}$	25.5	3833	2525	0.042	1
866(3)	C ₁₂ H ₂₀ CuN ₂ O ₁₂	447.84	1.72	2	452	P2 ₁	13.8	3433	1302	0.087	2
742(1)	C ₁₂ H ₁₀ Cl ₂ CuN ₂ O ₆	412.67	1.84	2	410	P2 ₁ /c	19.2	2000	1107 ^b	0.050	3
1392(1)	C ₁₂ H ₁₂ CuN ₂ O ₈	375.78	1.79	4	756	C2/c	16.8	2924	1477	0.047	4
581(1)	C ₂₂ H ₂₂ Cu ₂ N ₄ O ₈	533.98	1.53	1	275	P $\bar{1}$	10.2	2338	1886	0.040	4
1664(1)	C ₂₄ H ₃₂ Cu ₃ N ₄ O ₂₁	903.17	1.80	2	918	P2/c	20.7	2962	1962	0.044	5
753(1)	C ₁₂ H ₁₆ CoN ₂ O ₁₀	407.20	1.79	2	418	P2 ₁ /c	12.51	2743	1591	0.049	6
741(1)	C ₁₂ H ₁₆ N ₂ NiO ₁₀	406.97	1.82	2	420	P2 ₁ /c	13.75	1050	627	0.117	6

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

^b I>2.5σ(I)

The intensities for the complexes were collected by $\theta/2\theta$ -technique with a scan rate varying from 1.0 or 1.5 to 15.0 or 20.0° min⁻¹ depending on the peak intensity, except for [Cu(N-nicO)₂(H₂O)₂]·4H₂O where the ω -scan technique was used with a scan rate varying from 4.0 to 29.3° min⁻¹.

After centering the crystals of [Cu(N-nicO)₂(H₂O)₂]-4H₂O and [Cu(N-inicO)₂(H₂O)₂(py)₂] were coated with glue to prevent decomposition.

The intensities of one or two standard reflections were recorded to monitor the crystal stability. This remained essentially constant throughout the data collection, except for [Cu(N-nicO)₂(H₂O)₂]·4H₂O where the intensity of the standard reflection decreased by 43 per cent during the data collection. The data was not corrected for decomposition. Reflections having $I > 3\sigma(I)$ except $I > 2.5\sigma(I)$ for [CuCl₂(N-nicOH)₂], were accepted into the structure analysis. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption or extinction was applied.

2.4. Structure Determination

Structures were solved by direct methods combined with Fourier syntheses. The hydrogen atoms were located from difference Fourier maps, except those of [Cu(N-nicO)₂(H₂O)₂]·4H₂O, which we did not attempt to locate, and

two hydrogen atoms of $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ whose positions were calculated. The atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann²⁵ and for hydrogen atoms those reported by Stewart *et al.*²⁶ The anomalous dispersion correction for copper was included in calculations of the trinuclear copper(II) complexes $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$.²⁷ The final R value ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) varied from 0.040 to 0.087.

Although the data for $[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ were not sufficient because of the poor crystal quality the structure was solved by refining the atomic coordinates of the isomorphous compound $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$. This refinement led to a final R -value of 0.117.

The calculations were carried out with *MULTAN*²⁸ and *X-Ray System*²⁹ programs on a Univac 1100 computer.

3. RESULTS AND DISCUSSION

3.1. Coordination around the Metal Ion

The main features of the structures and coordination around the metal ion have been presented for the complexes of nicotinic acid N-oxide $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$, $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, $[\text{CuCl}_2(\text{N-nicoH})_2]$, $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ and $[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ and for the Cu(II) complexes of isonicotinic acid N-oxide, $[\text{Cu}(\text{N-inicO})_2-$

Table 2. Interatomic distances(Å) with their standard deviations in environments of the central metal atoms.

Complex	M-M	M-O(aqua)	M-O(μ -OH)	M-O(COO)	M-O(μ -COO)	M-O(N-O)	M-N(ring)	M-Cl	Ref.
[Cu ₃ (N-nicO) ₄ (OH) ₂ (H ₂ O) ₂]	3.035(1)	1.925(1)	1.912(2) 1.876(1)	1.943(2)	1.954(1) 1.979(2)	2.426(2) 2.672(1)			1
[Cu(N-nicO) ₂ (H ₂ O) ₂] \cdot 4H ₂ O		1.866(6) 2.000(6)		1.926(5) 1.957(4)		2.577(6) 2.468(6)			2
[CuCl ₂ (N-nicOH) ₂]						1.962(3)		2.241(1)	3
[Cu(N-inicO) ₂ (H ₂ O) ₂]		1.930(2)			1.934(4) 2.691(4)				4
[Cu(N-inicO) ₂ (H ₂ O) ₂ (py) ₂]		2.509(1)		1.973(1)			2.006(1)		4
[Cu ₃ (N-inicO) ₄ (OH) ₂ (H ₂ O) ₅] \cdot 2H ₂ O	3.365(1)	2.260(4) 1.987(3) 2.247(3)	1.895(2) 1.909(3)	1.954(2)	1.979(3) 1.978(2)				5
[Co(N-nicO) ₂ (H ₂ O) ₄]		2.072(1) 2.113(2)		2.102(1)					6
[Ni(N-nicO) ₂ (H ₂ O) ₄]		2.05(2) 2.05(2)		2.03(2)					6

Table 3. Coordination geometry and coordination angles ($^{\circ}$) with their standard deviations around the central metal.

Complex	Central metal	Coordination geometry	Angle	Ref.	
$[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$	Cu(1)	elongated octahedral	O(OH)-Cu-O(COO)	87.28(7)	1
			O(NO)-Cu-O(COO)	89.46(7)	
			O(NO)-Cu-O(OH)	87.98(7)	
	Cu(2)	square pyramidal	O(COO)-Cu-O(COO)	153.73(7)	
			O(COO)-Cu-O(H ₂ O)	84.55(5)-84.84(6)	
			O(COO)-Cu-O(OH)	92.27(5)-97.55(6)	
			O(NO)-Cu-O(COO)	95.26(7)-103.56(7)	
			O(NO)-Cu-O(H ₂ O)	92.37(6)	
			O(NO)-Cu-O(OH)	89.84(6)	
			O(H ₂ O)-Cu-O(OH)	176.28(6)	
$[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	Cu	elongated octahedral	O(COO)-Cu-O(COO)	175.8(2)	2
			O(COO)-Cu-O(H ₂ O)	87.4(2)-93.5(2)	
			O(H ₂ O)-Cu-O(H ₂ O)	175.6(3)	
			O(NO)-Cu-O(NO)	178.9(2)	
			O(NO)-Cu-O(COO)	88.3(2)-92.8(2)	
			O(NO)-Cu-O(H ₂ O)	85.7(2)-94.6(2)	
			$[\text{CuCl}_2(\text{N-nicOH})_2]$	Cu	
$[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$	Cu	tetragonally distorted octahedral			O(COO)-Cu-O(COO)
			O(H ₂ O)-Cu-O(COO)	87.1(1)-88.8(1)	
$[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$	Cu	octahedral	N-Cu-O(COO)	88.63(3)	4
			N-Cu-O(H ₂ O)	92.39(2)	
			O(COO)-Cu-O(H ₂ O)	91.34(3)	

Table 3. continued

Complex	Central metal	Coordination geometry	Angle	Ref.	
[Cu ₃ (N-nicO) ₄ (OH) ₂ (H ₂ O) ₅]·2H ₂ O	Cu(1)	square pyramidal	O(COO)-Cu-O(OH)	85.97(11) - 92.74(11)	5
			O(COO)-Cu-O(H ₂ O)	94.53(9)	
			O(COO)-Cu-O(COO)	170.94(13)	
			O(OH)-Cu-O(H ₂ O)	98.19(8)	
			O(OH)-Cu-O(OH)	163.62(11)	
	Cu(2)	square pyramidal	O(COO)-Cu-O(COO)	168.52(14)	
			O(COO)-Cu-O(OH)	95.39(11) - 96.05(11)	
			O(COO)-Cu-O(H ₂ O)	84.26(11) - 88.16(11)	
			O(OH)-Cu-O(H ₂ O)	104.41(11) - 161.05(11)	
			O(H ₂ O)-Cu-O(H ₂ O)	94.52(11)	
[Co(N-nicO) ₂ (H ₂ O) ₄]	Co	octahedral	O(COO)-Co-O(H ₂ O)	87.06(6) - 88.09(6)	6
			O(H ₂ O)-Co-O(H ₂ O)	90.25(6)	
[Ni(N-nicO) ₂ (H ₂ O) ₄]	Ni	octahedral	O(COO)-Ni-O(H ₂ O)	87.2(7) - 88.1(7)	6
			O(H ₂ O)-Ni-O(H ₂ O)	90.2(7)	

$(\text{H}_2\text{O})_2$], $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ in papers 1 - 6, and are only summarized here.

Interatomic distances and angles with estimated standard deviations in the central metal environments are presented in Tables 2 and 3.

3.1.1. Trinuclear copper(II) complexes

General remarks

A great number of trinuclear oxygen-bridged Cu(II) complexes have been described in the literature. Structures with halide or phosphino bridges are known as well. Trinuclear Cu(II) complexes can be classified into linear and triangular complexes according to the position of the copper atoms relative to one another. The copper atoms have characteristic environments in both the linear and triangular complexes.

Linear trinuclear Cu(II) complexes characteristically display 1) oxygen bridges between copper atoms, with a Cu_3O_4 core,^{1,30,31} 2) oxygen bridges and carboxylato bridges,^{1,32} or 3) chloro bridges between copper atoms, with a Cu_3Cl_4 core.³³⁻³⁵

Triangular oxygen-bridged Cu complexes characteristically display 1) an equilateral triangle formed by three copper atoms, with a bridging μ_3 -oxygen and a Cu_3O

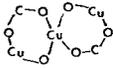
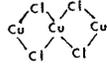
unit,³⁶⁻³⁹ 2) μ_2 -oxygen-bridged copper atoms forming an almost planar Cu_3O_3 ring,⁴⁰⁻⁴¹ 3) μ_2 -oxygen-bridged copper atoms with a Cu_3O_2 core,⁴²⁻⁴⁵ or 4) μ_2 -hydroxo- and carboxylato-bridged copper atoms forming two Cu-O-Cu-O-C-O rings.⁵

In addition, a triangular arrangement of the copper atoms has been in di- μ -|bis(diphenylphosphino)methane|- μ -iodo-di- μ_3 -iodo-tricopper(I) 0.5dichloromethane with phosphino, μ - and μ_3 -iodo bridges.⁴⁶ And trinuclear Cu(II) complexes of guanosine 5'-phosphate with phosphate bridges have been described.^{47,48}

Structural data of trinuclear Cu(II) complexes, including their Cu-Cu distances, are collected in Tables 4 and 5. In trinuclear complexes the environments of all three copper atoms may be the same, two may be the same or all may be different.

The most usual coordination environments of copper atoms are square-pyramidal (4+1) and square-planar arrangements, generally distorted in some way. In several complexes the central metal atom has been found to have distorted octahedral coordination geometry.^{1,32-34,42} In di- μ -(1,3,-diamino-2-propanolato)bis(1,3-diamino-2-propanol)tricopper(II) nitrite all three copper atoms have octahedral environment.⁴⁵

Table 4. Some structural data for linear trinuclear oxygen- or halogen-bridged Cu(II) complexes.

Core	Complex	Coordination geometry ^a	Cu-Cu (Å)	Cu-O(bridged) (Å)	Cu-Cl (Å)	Cu-O-Cu (°)	Cu-Cl-Cu (°)	O-Cu-O (°)	Cl-Cu-Cl (°)	Ref.
Cu ₃ O ₄	[Cu ₃ (C ₁₁ H ₁₉ N ₂ O ₂) ₂]	square planar	3.017(1)	1.91-1.96		102.4		78.1-76.0		30
	[Cu ₃ (C ₁₈ H ₄₂ N ₂ O ₂)(OH) ₂] ⁻ (C ₁₀ H ₄) ₂	square planar tetragon. pyramidal	2.902(1)	1.913(7)- 1.907(7)		98.6(3)- 99.1(3)		79.0(3)- 79.3(3)		31
Cu ₃ O ₆ C ₂	[Cu ₃ (C ₁₀ H ₂₂ NO) ₂ - (C ₇ H ₅ O ₂) ₄ (C ₂ H ₆ O) ₂]	octahedral square planar	3.211(6)	1.97(2)- 1.95(1)		111(1)		91.1(6)		32
	[Cu ₃ (C ₆ H ₄ NO ₃) ₄ (OH) ₂ - (H ₂ O) ₂]	octahedral square pyramidal	3.035(1)	1.933(2)- 1.928(2)		106.45(7)		87.28(7)		1
Cu ₃ Cl ₄	[Cu ₃ Cl ₆ (C ₆ H ₇ NO) ₂ (H ₂ O) ₂] ^b	octahedral square pyramidal	3.581(2) 3.255(3) ^c	2.00(1)	2.523(4)	109.3(5)	93.1(1)- 86.3(1)	70.7(4)	84.4(1)- 92.8(1)	33
	[Cu ₃ Cl ₈ (C ₁₀ H ₁₂ N ₁₀) ₂ - 4H ₂ O] ^d	octahedral square pyramidal	3.479(2) 3.274(3) ^c		2.534(3)- 2.540(3)				92.0(1)- 91.7(1)	34
	[Cu ₃ Cl ₆ (H ₂ O) ₂]- 2H ₈ C ₄ S ₂ O ₂ ^d	square planar	3.331(4) 3.928(2) ^c		2.295(4)- 2.287(4)		92.7(2)- 93.8(2)		91.7(1)- 96.2(1)	35

^aCoordination geometry of the central copper atom is tabulated first. ^bN=O oxygen bridges to the copper atoms of adjacent units. ^cThe distance between the copper atoms of adjacent units. ^dChloro-bridges between adjacent units.

Table 5. Some structural data for triangular trinuclear oxygen-bridged Cu(II) complexes.

Core	Complex	Coordination geometry	Cu-Cu (Å)	Cu-Cu-Cu (°)	Cu-O(μ_3, ν) (Å)	Cu-O-Cu (°)	O-Cu-O	Ref.
Cu_3O	$[\text{Cu}_3(\text{C}_6\text{H}_5\text{N}_2\text{O})_3(\text{OH})\text{SO}_4] \cdot 16.3\text{H}_2\text{O}$	tetragon. pyramidal	3.220(3)		1.99(1)	108.2(4)		36,37
	$[\text{Cu}_3(\text{C}_8\text{H}_{17}\text{N}_2\text{O})_3(\text{H}_2\text{O})_3\text{OH}_3] \cdot (\text{ClO}_4)_{3/2} \cdot (\text{H}_2\text{O})_4$	square pyramidal	3.246(3)		1.97(1)	110.9(4)		38
	$[\text{Cu}_3\text{OH}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O})_3(\text{ClO}_4)] \text{ClO}_4$	tetrahedral			1.964(5)	108.8(3)		39
Cu_3O_3	$[\text{Cu}_3(\text{C}_3\text{H}_9\text{N}_2\text{O})_3(\text{C}_3\text{H}_{12}\text{N}_2\text{O}_2)_3] \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	square pyramidal square planar	3.420(3) 3.450(6) 3.694(3)		1.965(9)	127.8(5)	94.8(4)	41
	$[\text{Cu}_3(\text{C}_3\text{H}_8\text{N}_2\text{O})_3](\text{NO}_3)_3$	square pyramidal square planar	3.321(2) 3.458(3)		1.95(9)	127.4(4)	96.4(4)	40
Cu_3O_2	$[\text{Cu}_3(\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	octahedral planar	3.053(2) 2.993(2)	97.3(4)	1.909(5)			42
	$[\text{Cu}_3(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$	trigonal bi-pyramidal	2.950(5) 2.975(5)	156.2(4)	1.89(1)			42
	$[(\text{C}_3\text{H}_{10}\text{N}_2\text{O})\text{Cu}(\text{C}_3\text{H}_9\text{N}_2\text{O})_2\text{Cu}] \cdot (\text{SCN})_4$	square pyramidal	3.400(3) 3.296(3)		1.968(10)	116.6(5)		43
	$[\text{Cu}_3(\text{C}_3\text{H}_8\text{N}_2\text{O})_2(\text{C}_3\text{H}_9\text{N}_2\text{O})_2] \text{I}_4 \cdot \text{CH}_3\text{OH}$	square planar			1.96(1)- 2.02(1)	114.4(6)- 118.2(6)		44
	$[\text{Cu}_3(\text{C}_3\text{N}_4\text{O})_2(\text{C}_3\text{N}_4\text{OH})_2] \cdot 4\text{NO}_2$	octahedral	3.440(5) 3.441(4) 4.944(5) 3.413(5) 3.492(6) 4.923(5)		1.968(14)	121.9(7)	91.9(1)	45
					1.980(14)	121.3(6)	90.9(1)	
$\text{Cu}_3\text{O}_6\text{C}_2$	$[\text{Cu}_3(\text{C}_6\text{H}_4\text{NO}_3)_4(\text{OH}_2)(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	square pyramidal	3.365(1)		1.940(3)	124.4(1)	85.97(11) 95.39(11)	5
								

Di- μ -hydroxo- and carboxylato-bridged Cu(II) complexes

In trinuclear $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ two pyridine monocarboxylato N-oxide and two hydroxo ligands act as bridges between the central and terminal copper atoms. Two pyridine monocarboxylato N-oxide ligands are coordinated to the terminal copper atoms. In $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ one aqua ligand is joined equatorially to each of the terminal copper atoms, whereas in $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ one aqua ligand is coordinated equatorially and another axially to each of the terminal copper atoms and a fifth aqua ligand is coordinated axially to the central copper atom.

Schematic representations of the stereochemistries of the copper atoms in $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ are seen in Fig.1 a) and b), respectively.

The environment of the terminal copper(II) ions is similar in $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$. All copper atoms in both complexes are surrounded by an oxygen sphere, and all have five coordination (4+1) except the central copper ion of $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ which has (4+2) coordination. In $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ the central copper(II) ion is strongly bonded to four oxygen atoms in only slightly distorted square-planar arrangement. The Cu-O(hydroxo)

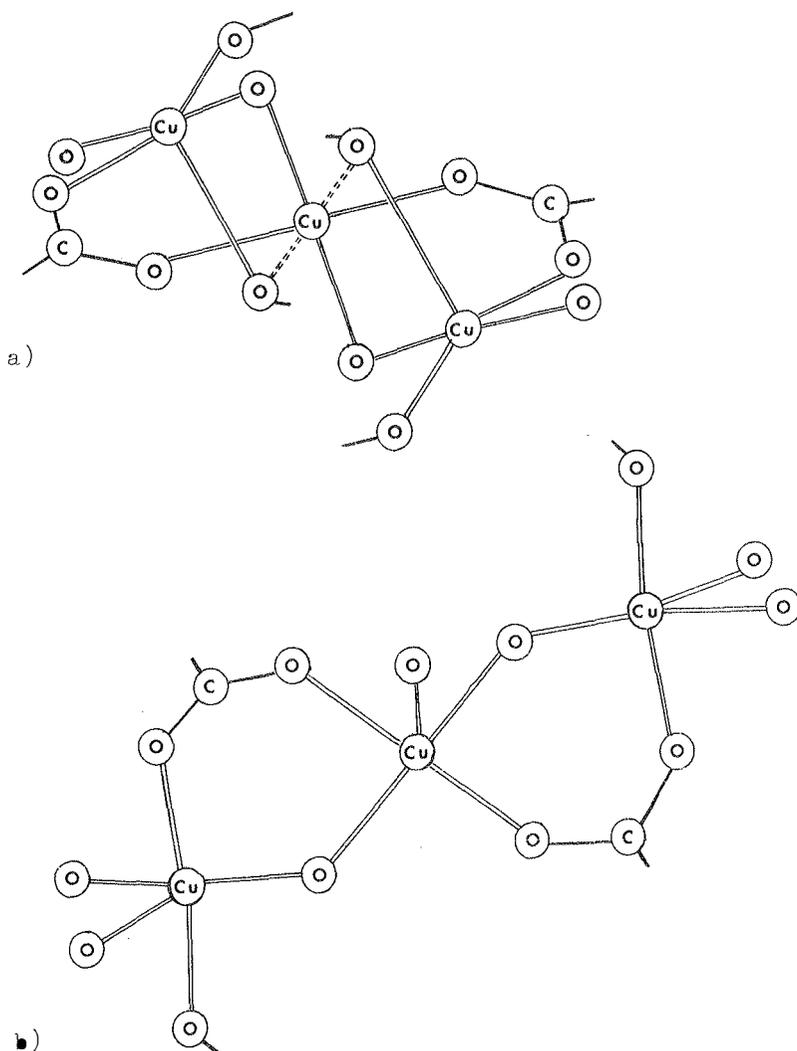


Fig. 1. Schematic representation of the environments of the copper atoms in a) $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and b) $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$.

bond is somewhat shorter than the Cu-O(carboxylato) bond and the angles deviate slightly from 90° . The coordination sphere of the copper(II) ion is completed by two N-oxide oxygen atoms of adjacent units at the long distances of 2.672(1) Å. The distance is equal to the sum of the corresponding van der Waals radii⁴⁹ indicating a weak interaction.

The coordination geometry of the terminal copper(II) ions is elongated distorted square pyramidal. The axial Cu-O(N-oxide) distance is 0.495 Å greater than the mean value of the basal Cu-O distances (1.931 Å). In addition to bond length distortion (1.876(1) - 1.979(2)) there is angle distortion as one oxygen atom, O(6) deviates 0.49 Å from the least-squares plane of Cu(2), O(3), O(7) and O(8) atoms. In $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ the central copper(II) ion is lifted 0.213 Å above the basal coordination plane towards the aqua ligand attached to it. The coordination environment is elongated distorted square pyramidal. The base coordination geometry of the terminal copper(II) ions is elongated square pyramidal, with the basal plane distorted towards tetrahedral coordination. The basal Cu-O bond distances vary between 1.909(3) and 1.987(3) Å. The angles are considerably distorted from the ideal ones. The deviations of oxygen atoms from the least-squares plane are 0.169-0.199 Å. The copper(II) ions are lifted 0.136 Å towards the axial aqua ligands. The axial Cu-O(aqua) bond lengths are about 0.31 Å greater than the mean value of the basal Cu-O bond

lengths (1.950(3) Å).

In both trinuclear complexes copper(II) ions are joined by two hydroxo oxygen and two carboxylato bridges forming two  six-membered rings. In addition, in $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ there are N-oxide oxygen-bridges between copper(II) ions.

A similar six-membered ring array is found in linear trinuclear bis(μ -benzoato- O,O')-bis(benzoato)-bis[μ -(2-dibutylaminoethanolato)]-bis(ethanol)tricopper(II), where the oxygen bridges are from the aminoalcohol ligand and the carboxylato group of the benzoate ligand.³² Some structural data for trinuclear Cu(II) complexes with carboxylato bridges are presented in Table 6. Several di-, tetra- and polynuclear copper complexes with carboxylato bridges are known and have been studied intensively.^{50,51} The bridging Cu-O-C-O-Cu distance, which is almost constant at 6.44 Å for the CuO_5 chromophore in dinuclear Cu(II) carboxylates,⁵⁰ is somewhat shorter in $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ and longer in $[\text{Cu}_3(\text{C}_{10}\text{H}_{22}\text{NO})_2(\text{C}_7\text{H}_5\text{O}_2)_4(\text{C}_2\text{H}_6\text{O})_2]$.³² The angles O-C-O compare well with the corresponding angles in dinuclear Cu(II) carboxylates (113-129.0°).⁵⁰

Cu-O(μ -hydroxo) bond distances, mean values 1.894(2) and 1.902(3) Å for $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$, respectively, are shorter than other Cu-O bond distances in the basal plane (mean values 1.950(2) and 1.950(3), respectively) and are in

Table 6. Some structural data for trinuclear Cu(II) complexes with carboxylato bridges.

Complex	Cu-O-C-O-Cu bridge (Å)	Angle O-C-O (°)	Bridge Cu-O-Cu (Å)	Angle Cu-O-Cu (°)	Ref.
$[\text{Cu}_3(\text{N-nico})_4(\text{OH})_2(\text{H}_2\text{O})_2]$	6.424(2)	127.2(2)	3.788(2)- 5.098(2)	106.45(7) 72.89(7)	1
$[\text{Cu}_3(\text{N-inico})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	6.431(4)	129.4(3)	3.804(3)	124.4(1)	5
$[\text{Cu}_3(\text{C}_{10}\text{H}_{22}\text{NO})_2(\text{C}_7\text{H}_5\text{O}_2)_4(\text{C}_2\text{H}_6\text{O})_2]$	6.50	123(2)	3.89	111(1)	32

good agreement with the Cu-O(μ -hydroxo) distances 1.922(7) and 1.904(7) Å in the linear trinuclear copper(II) complexes reported by Matsumoto *et. al.*³¹ They are also comparable with the corresponding Cu-O(hydroxo) distances of dinuclear di- μ -hydroxo Cu(II) complexes,⁵²⁻⁶⁴ but clearly shorter than the Cu-O(μ_3 -hydroxo) bond lengths (1.99³⁷, 1.97³⁸ and 1.964²⁴Å) in trinuclear Cu(II) complexes. The mean values of the Cu-O(bridged) bond distance are 1.94 and 1.96 Å for linear and triangular trinuclear Cu(II) complex, respectively.

The angle Cu-O-Cu is 106.45(7)^o in [Cu₃(N-nicO)₄(OH)₂-(H₂O)₂] and much wider, 124.4(1)^o, in [Cu₃(N-inicO)₄(OH)₂-(H₂O)₅].2H₂O. In linear trinuclear Cu(II) complexes the mean value of the corresponding angle is 104.5^o. It is smallest (98.6-102.4^o) in complexes with the core Cu₃O₄, Cu_OCu_OCu.^{30,31} The angle O-Cu-O of these complexes is also rather small (76.0-79.3^o). The smallest value (70.4(4)^o) is found in [Cu₃Cl₆(C₆H₇NO)₂(H₂O)₂]³³ and the mean value is 82.9^o.

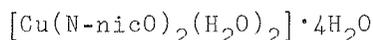
The mean value of 118.2^o for the angle Cu-O-Cu in triangular Cu(II) complexes is considerably greater than the corresponding angles in linear Cu(II) complexes. The angle is smallest in μ_3 -O(H)-complexes (108.2-110.9^o)³⁶⁻³⁹ and greatest in complexes having a Cu₃O₃ six-membered ring (117.2-139.5^o).^{40,41}

In linear oxo-bridged complexes the Cu-Cu separation varies between 2.902(1) and 3.211(6) Å, being larger for chloro-bridged complexes (3.255(3)-3.928(2) Å).

The Cu—Cu separation is 2.975(5)-3.694(3) Å for triangular complexes. In $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ the corresponding values are 3.035(1) and 3.211(6) Å, respectively.

3.1.2. Mononuclear copper(II) complexes

The stereochemistries of the copper(II) ions in $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, $[\text{CuCl}_2(\text{N-nicOH})_2]$, $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ are schematically represented in Fig. 2.



$[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ is a polymeric complex with double nicotinato N-oxide bridges joined through one carboxylato oxygen atom and the N-oxide oxygen atom to the copper(II) ions. There is an oxygen sphere around each copper(II) ion. The copper(II) ion adopts a Jahn-Teller distorted octahedral geometry (4+2). The equatorial oxygen atoms are from two aqua groups and two carboxylate groups of nicotinate N-oxide at distances 1.866(6)-2.000(6) Å. Polymerization occurs through N-oxide oxygen atoms joined to the axial coordination sites of copper(II) ion. The long Cu—O distances 2.468(6) and 2.577(6) Å indicate a weak interaction. The Cu—O bond distances are in good agreement with the corresponding

values in $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$.

$[\text{CuCl}_2(\text{N-nicOH})_2]$

The complex molecules of $[\text{CuCl}_2(\text{N-nicOH})_2]$ are made up of two chloride ions and of two nicotinic acid N-oxide ligands coordinating through the oxygen atom of the N-oxide group. The copper(II) ion has a distorted square-planar coordination geometry. The carboxylic oxygen atoms of adjacent molecules could be considered to complete the coordination sphere of the copper(II) ion. However, the wide separation of 3.082(4) Å, 0.4 Å greater than the sum of the corresponding van der Waals radii, indicates a very weak interaction.

The Cu-O(N-oxide) distance 1.962(3) Å compares well with the corresponding Cu-O bond lengths in Cu(II) complexes of pyridine N-oxides^{33,65-68} but is much shorter than Cu-O(N-oxide) distances in other studied Cu(II) complexes of nicotinic acid N-oxide, where N-oxide oxygens have joined axially to the copper(II) ions and the geometry is Jahn-Teller distorted square pyramidal or octahedral.

The Cu-Cl distance 2.241(1) Å agrees well with the values presented for the complexes of copper(II) chloride with pyridine N-oxides: 2.20-2.27 Å^{33,65-67,69,70} and one extreme value of 2.515.⁶⁸ When the chloride ion acts as a bridging ligand the distance to the other copper atom is generally longer: 2.955 Å in catena-bis(μ -(2-

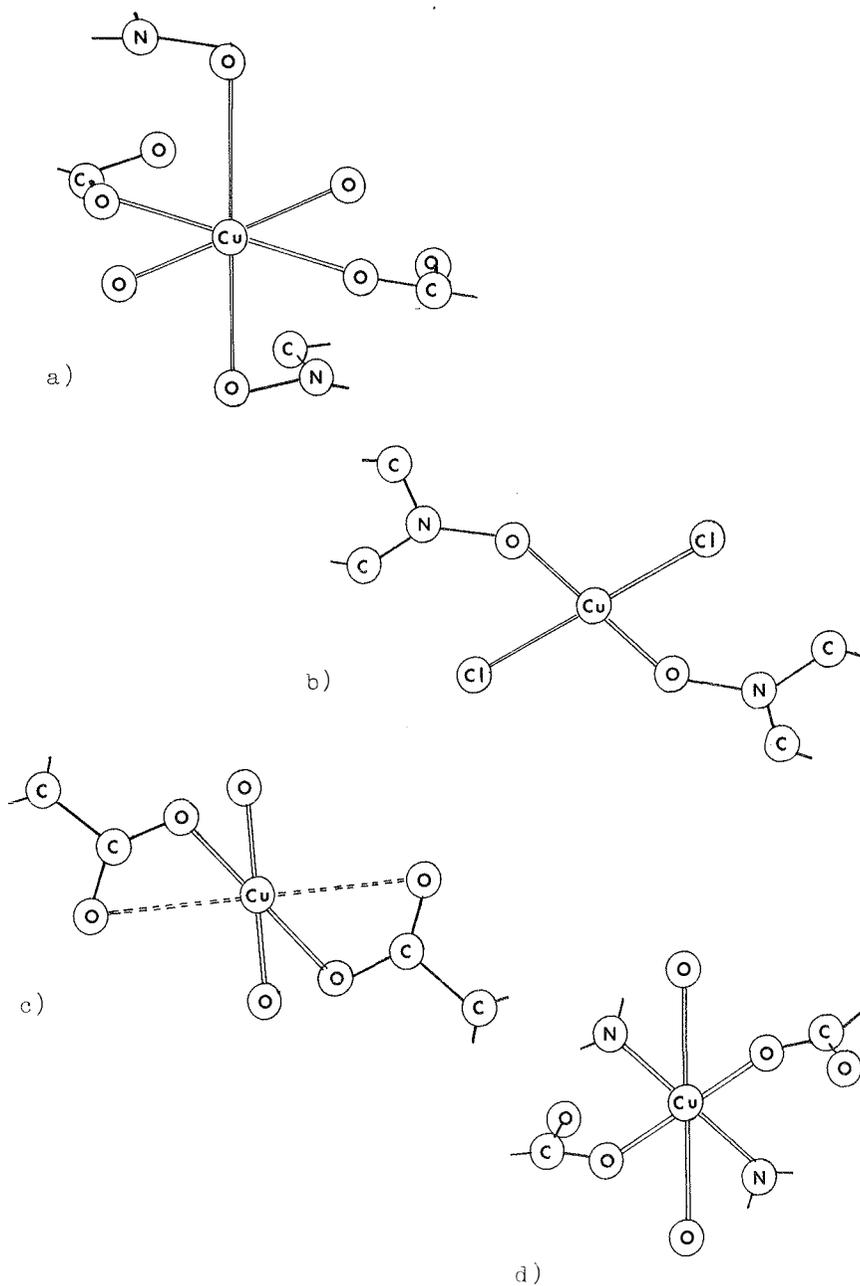
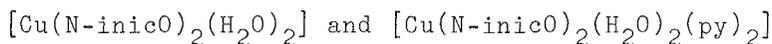


Fig. 2. Schematic representation of the stereochemistries of the copper(II) ion in a) $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, b) $[\text{CuCl}_2(\text{N-nicOH})_2]$, c) $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ and d) $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$.

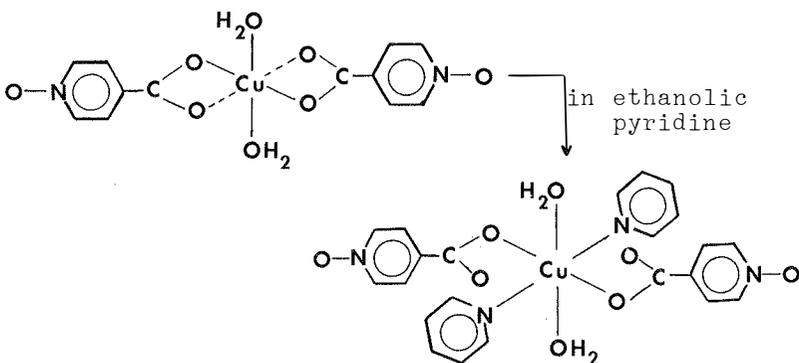
picoline N-oxide)-chlorocopper(II)-di- μ -chloro)diaqua-copper(II)³³ and 2.836(5) Å in di- μ -(pyridine N-oxide)-bis(dichlorocopper(II)),⁷⁰ for instance.



$[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ consists of two isonicotinato N-oxide and two aqua ligands coordinated to the copper(II) ion. Isonicotinato N-oxide chelates to the copper atom through both carboxylato oxygen atoms, forming a Cu-O-C-O four-membered ring. The copper atom deviates 0.245 Å from the planar C-C $\begin{matrix} \nearrow \text{O} \\ \searrow \text{O} \end{matrix}$ group. The angle O-Cu-O formed by the carboxylato oxygen atoms and the copper atom has narrowed to 54.8(1)^o, and is in good agreement with complexes having a similar coordination of the carboxylato group.⁷¹⁻⁷⁴ The aqua oxygen atoms and two oxygen atoms of the carboxylato groups form a square plane around the copper(II) ion with equal bond lengths, 1.930(2) and 1.934(4) Å. The other two, "out-of-plane" Cu-O(carboxylato) distances are long, 2.691(4) Å, corresponding to the sum of the van der Waals radii.⁴⁹ The angle between this Cu-O distance and the least-squares plane of the copper and both carboxylato oxygen atoms is 35.5^o.

When the "out-of-plane" oxygen atoms are considered as taking part in the coordination the environment of copper is regarded as an extremely tetragonally distorted octahedron. The transforming of $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ into a pyridine derivative upon recrystallization in ethanolic

pyridine solution and the structure of this derivative $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ confirm the (4+2) coordination of $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2]$.



When in the derivative two additional pyridine ligands join to the coordination sphere of copper(II) ion by the nitrogen atoms, the long Cu-O(carboxylato) separation increases from 2.691(4) to 3.251(1) Å and the angle O-C-O of the carboxylato group increases from 125.0(4)^o to 127.1(1)^o. The Cu-N bond length is 2.001(1) Å. The pyridine ligands do not replace the aqua ligands, but the Cu-O(aqua) distances increase from 1.930(2) to 2.509(1) Å, the coordination geometry of $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ being a typical elongated octahedron.

3.1.3. Cobalt(II) and nickel(II) complexes

The isomorphous complex molecules of $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ and $[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ are made up of two nico-

tinato N-oxide and four aqua ligands joined to the central metal atom. The nicotinato N-oxide ligand is coordinated monodentately by the carboxylato oxygen atom to the common octahedral coordination sphere of the Co or Ni atom. The Co-O bond lengths 2.072(1)-2.113(2) Å are in good agreement with the corresponding bond lengths 2.061(1)-2.148(1) Å and 2.052(2)-2.092(2) Å in $[\text{Co}(\text{N-picO})_2(\text{H}_2\text{O})_2]^{21}$ and $[\text{Co}(\text{H}_2\text{O})_6](\text{N-inicO})_2$,²³ respectively.

3.2. Nicotinate and isonicotinate N-oxide ligand

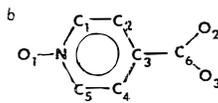
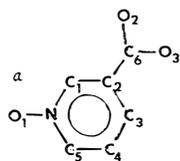
Bond distances and angles in pyridine N-oxide groups and carboxylate groups are presented for the studied complexes of nicotinic and isonicotinic acid N-oxides in Tables 7,8 and 9,10, respectively.

The mean value of the N-C bond distances in the pyridine ring is 1.348 Å for nicotinato N-oxide and 1.351 Å for isonicotinato N-oxide and the mean C-C bond distances are 1.379 and 1.385 Å, respectively. The mean angles in the pyridine ring of nicotinato and isonicotinato N-oxides are C-N-C 121.4°, 121.9°, N-C-C 120.0°, 120.0° and C-C-C 119.5°, 119.3°, respectively.

The coordination of the N-oxide oxygen atom does not seem to influence the N-O bond length: in the uncoordinated N-O groups of nicotinato N-oxide complexes bond distances vary from 1.327(3) to 1.347(2) Å, and in the coordinated groups from 1.322(2) to 1.352(4) Å.

Table 7. Interatomic distances (Å) with their standard deviations in pyridine N-oxide groups for the complexes of nicotinic acid N-oxide^a and isonicotinic acid N-oxide^b.

Complex	N-O ₁		N-C ₁	N-C ₅	C ₁ -C ₂	C ₂ -C ₃	C ₃ -C ₄	C ₄ -C ₅	Ref
	uncoord.	coord.							
[Cu ₃ (N-nicO) ₄ (OH) ₂ (H ₂ O) ₂] ^c	1.327(3)	1.322(2)	1.348(3)	1.336(3)	1.374(3)	1.363(3)	1.387(3)	1.361(3)	1
[Cu(N-nicO) ₂ (H ₂ O) ₂]·4H ₂ O ^c		1.333(8)	1.390(8)	1.347(10)	1.362(10)	1.401(11)	1.431(10)	1.390(11)	2
[CuCl ₂ (N-nicOH) ₂]		1.352(4)	1.343(5)	1.342(7)	1.365(6)	1.386(7)	1.359(6)	1.367(7)	3
[Co(N-nicO) ₂ (H ₂ O) ₄]	1.347(2)		1.344(2)	1.331(2)	1.384(2)	1.379(3)	1.379(3)	1.381(3)	6
mean value	1.337	1.336	1.348			1.379			
[Cu(N-inicO) ₂ (H ₂ O) ₂]	1.337(5)		1.371(6)	1.355(6)	1.369(8)	1.398(7)	1.404(7)	1.379(7)	4
[Cu(N-inicO) ₂ (H ₂ O) ₂ (py) ₂]	1.314(1)		1.355(1)	1.344(1)	1.371(2)	1.379(1)	1.385(1)	1.376(2)	4
[Cu ₃ (N-inicO) ₄ (OH) ₂ (H ₂ O) ₅]·2H ₂ O	1.340(4)		1.345(6)	1.339(5)	1.395(5)	1.389(5)	1.389(6)	1.381(5)	5
mean value	1.330		1.351			1.385			



^c only mean values are tabulated where more than one chemically equivalent angle is present (estimated standard deviations in parentheses are average e.d.s's for an individual distance)

Table 8. Bond angles ($^{\circ}$) with their standard deviations in pyridine N-oxide groups for the complexes of nicotinic acid N-oxide and isonicotinic acid N-oxide.

Complex	O ₁ -N-C ₁	O ₁ -N-C ₅	C ₁ -N-C ₅	N-C ₁ -C ₂	C ₄ -C ₅ -N	C ₁ -C ₂ -C ₃	C ₂ -C ₃ -C ₄	C ₃ -C ₄ -C ₅	Ref.
[Cu ₃ (N-nicO) ₄ (OH) ₂ (H ₂ O) ₂]	118.9(2) 120.4(2)	120.1(2) 118.9(2)	120.9(2) 120.6(2)	120.2(2) 120.1(2)	120.4(2) 120.6(2)	119.9(2) 119.5(2)	118.8(2) 119.2(2)	119.8(2) 119.7(2)	1
[Cu(N-nicO) ₂ (H ₂ O) ₂] \cdot 4H ₂ O	125.5(6) 108.8(5)	120.3(5) 121.9(5)	114.1(6) 129.2(6)	125.0(6) 109.9(6)	125.4(7) 119.8(6)	122.7(6) 123.9(6)	120.4(7) 116.0(6)	112.0(8) 121.1(6)	2
[CuCl ₂ (N-nicOH) ₂]	119.2(4)	118.7(3)	122.1(4)	119.9(4)	118.9(4)	119.0(4)	119.5(4)	120.6(5)	3
[Co(N-nicO) ₂ (H ₂ O) ₄] <i>mean value</i>	119.0(1) 119.3	119.1(1)	121.9(2) 121.4	120.2(1)	119.7(2) 120.0	119.0(2)	119.4(2) 119.5	119.9(2)	6
[Cu(N-inicO) ₂ (H ₂ O) ₂]	120.4(4)	117.5(4)	122.0(4)	120.0(4)	119.6(4)	119.2(4)	119.7(4)	119.4(4)	4
[Cu(N-inicO) ₂ (H ₂ O) ₂ (py) ₂]	119.5(1)	120.1(1)	120.4(1)	120.3(1)	120.5(1)	120.3(1)	118.3(1)	120.0(1)	4
[Cu ₃ (N-inicO) ₄ (OH) ₂ (H ₂ O) ₅] \cdot 2H ₂ O <i>mean value</i>	119.9(3) 116.4(3) 119.0	118.4(3) 120.1(3)	121.7(3) 123.5(3) 121.9	121.0(3) 117.7(4) 120.0	120.0(4) 120.9(4)	117.0(4) 120.4(4)	120.4(3) 120.8(3) 119.3	119.9(3) 116.7(4)	5

Table 9. Interatomic distances (Å) with their standard deviations in carboxylato group.

Complex	C(ring)-C	Monodentate COO		Bridging COO	Uncoordinated COOH		Ref.
		C-O	C-O(coord.)	C-O	C-OH	C=O	
$[\text{Cu}_3(\text{N-nico})_4(\text{OH})_2(\text{H}_2\text{O})_2]$	1.504(3)	1.208(2)	1.262(2)	1.240(2) 1.250(3)			1
$[\text{Cu}(\text{N-nico})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$	1.549(9)	1.261(9)	1.228(9)				2
$[\text{CuCl}_2(\text{N-nicoH})_2]$	1.490(6)				1.315(7)	1.190(6)	3
$[\text{Co}(\text{N-nico})_2(\text{H}_2\text{O})_4]$	1.508(2)	1.249(2)	1.260(2)				6
$[\text{Cu}(\text{N-inico})_2(\text{H}_2\text{O})_2]$	1.509(6)			1.229(6) ^a 1.286(5) ^a			4
$[\text{Cu}(\text{N-inico})_2(\text{H}_2\text{O})_2(\text{py})_2]$	1.510(1)	1.228(1)	1.269(1)				4
$[\text{Cu}_3(\text{N-inico})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$	1.541(5)	1.218(6)	1.284(5)	1.215(5) 1.259(4)			5

^a chelating

Table 10. Bond angles with their standard deviations ($^{\circ}$) in carboxylate groups. (ring) $C-C_6 \begin{matrix} \nearrow O_2 \\ \searrow O_3 \end{matrix}$

Complex	$O_2-C_6-O_3$		$M-O_2-C_6$		$M-O_3-C_6$	$O_2-C_6-C(\text{ring})$		$O_3-C_6-C(\text{ring})$		Ref.
	monodent.	bident.	monodent.	bident.	bident.	monodent.	bident.	monodent.	bident.	
$[Cu_3(N-nico)_4(OH)_2(H_2O)_2]$	126.2(2)	127.2(2) ^a	129.1(1)	129.8(2)	126.4(1)	119.5(2)	115.8(2)	114.3(1)	116.9(2)	1
$[Cu(N-nico)_2(H_2O)_2] \cdot 4H_2O$ ^b	128.8(6)		127.8(4)			115.2(6)		115.9(7)		2
$[CuCl_2(N-nicoH)_2]$ ^c	124.9(4)					112.4(4)		122.6(5)		3
$[Co(N-nico)_2(H_2O)_4]$	126.1(2)		125.3(1)			116.1(1)		117.8(1)		6
$[Cu(N-inico)_2(H_2O)_2]$ ^d		125.0(4)		73.2(3)	106.8(3)		119.5(4)		115.5(4)	4
$[Cu(N-inico)_2(H_2O)_2(py)_2]$	127.06(10)		126.84(7)			114.05(8)		118.87(8)		4
$[Cu_3(N-inico)_4(OH)_2(H_2O)_5] \cdot 2H_2O$	128.7(3)	129.4(3) ^a	125.5(2)	129.7(3)	130.9(3)	112.1(4)	117.4(3)	119.3(4)	113.2(4)	5

^a bridging COO, ^b only mean values are tabulated where more than one chemically equivalent angle is presented (estimated standard deviations in parentheses are average e.s.d.'s for an individual distance).

^c uncoordinated COOH, ^d chelating COO.

In isonicotinato N-oxide ligands the N-O bond distances of uncoordinated N-oxide groups vary from 1.314(1) to 1.340(4) Å. The mean value of the angle O-N-C is 119.3° for nicotinato N-oxide ligand and 119.0° for isonicotinato N-oxide ligand.

The C(ring)-C bond distance in the complexes of nicotinic acid N-oxide varies from 1.490(6) Å in [CuCl₂-(N-nicOH)₂] to 1.549(9) Å in [Cu(N-nicO)₂(H₂O)₂].4H₂O, and the mean bond length is 1.513 Å. The C(ring)-C bond length for the isonicotinato N-oxide ligands varies from 1.509(6) Å in [Cu(N-inicO)₂(H₂O)₂] to 1.541(5) Å in [Cu₃(N-inicO₄(OH)₂(H₂O)₅].2H₂O, with a mean length of 1.520 Å.

The carboxylate and N-oxide groups of pyridine monocarboxylate N-oxides compete for the coordination sites of the central metal atom. In pyridine N-oxide complexes the N-oxide oxygen atom may be attached with normal Cu-O bond lengths^{21,65} or be loosely attached at a long distance to the metal ion.⁶⁹ It can also act as a bridge atom, allowing the formation of dinuclear^{66,68} or polynuclear complexes.^{33,67,70} The carboxylate group can exist in ionic form in a structure or be coordinated mono- or bidentately, by chelating and/or by bridging.

Only in the Cu(II) complexes of nicotinic acid N-oxide was the oxygen atom of the N-oxide group able to coordinate to the copper atom (Table 11).

The angle Cu-O-N varies from 108.8(4) to 125.8(1)°, whereas the theoretical angle is 120° if the oxygen atom is assumed to have sp² hybridization. The angle Cu-O-N

Table 11. Coordination of N-O group.

Complex	Bond distance (Å)		Angle (°)	Ref.
	Cu-O	N-O	Cu-O-N	
[Cu ₃ (N-nicO) ₄ (OH) ₂ (H ₂ O) ₂]	2.426(2)	1.322(2)	125.8(1)	1
	2.672(1)			
[Cu(N-nicO) ₂ (H ₂ O) ₂]·4H ₂ O	2.577(6)	1.345(8)	108.8(4)	2
	2.468(6)	1.321(7)	113.1(4)	
[CuCl ₂ (N-nicOH) ₂]	1.962(3)	1.352(4)	120.1(2)	3

is $116.1(1)^\circ$ in $[\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2]^{21}$ and $109.9\text{-}127.1^\circ$ in Cu(II) complexes of pyridine N-oxides.^{33,65,67-69}

In the uncoordinated carboxylic group of $[\text{CuCl}_2(\text{N-nicOH})_2]$, C-O bond distances are $1.190(6)$ Å for the double bond and $1.315(7)$ Å for the C-O(hydroxy) bond, comparable to the corresponding values of free nicotinic acid N-oxide $1.198(1)$ and $1.301(1)$ Å.⁷⁵ When the carboxylic group is coordinated the C-O bond distances increase, being greater in the monodentately bonded than the bridging carboxylato group except in $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$.

In $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ the nicotinato N-oxide ligands are coordinated bidentately, two of them bridging through both carboxylato oxygen atoms and two through one carboxylato oxygen and the N-oxide oxygen; weak Cu-O(N-oxide) bondings of $2.426(2)$ and $2.672(1)$ Å, connect the structural units together. Simultaneously the N-oxide oxygen acts as a bridge between central and terminal copper atoms.

In $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ the nicotinato N-oxide ligands form double bridges between copper(II) ions, coordinating through one carboxylato oxygen atom and N-oxide oxygen atom. Here, too, polymerization occurs through the Cu-O(N-oxide) bond ($2.468(6)$ - $2.577(6)$ Å).

In $[\text{CuCl}_2(\text{N-nicOH})_2]$ prepared in ethanolic solution, unprotonated nicotinic acid N-oxide appears as a monodentate ligand coordinating only through the N-oxide oxygen atom. Coordination is similar to that in dichlorobis(2,6-lutidine N-oxide)copper(II) and the Cu-O(N-oxide)

bond distances are comparable: 1.962(3) in our compound and 1.97(1)-1.93(1) Å, in the other.⁶⁵

The nicotinato N-oxide ligand acts monodentately in $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$ and $[\text{Ni}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$, coordinating through one carboxylato oxygen atom. In the isomorphous Co(II) and Ni(II) complexes of picolinic acid N-oxide the picolinato N-oxide ligand coordinates bidentately through one carboxylato oxygen atom and the N-oxide oxygen atom, forming a six-membered ring.²¹ The isonicotinate N-oxide group is not bonded at all to cobalt(II) and nickel(II) ions but exists in ionic form in the structures of $[\text{Co}(\text{H}_2\text{O})_6](\text{N-inicO})_2$ and $[\text{Ni}(\text{H}_2\text{O})_6](\text{N-inicO})_2$.²³

Isonicotinate N-oxide ligand is joined to the copper(II) ion only through the carboxylate group, coordinating in different ways. In trinuclear $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$ the carboxylato N-oxide ligands act as bridges between the central and terminal copper atoms, or attach monodentately to the terminal copper atoms. Isonicotinato N-oxide ligands also form bridges through their carboxylato groups in tetranuclear $[\text{Cu}_4(\text{N-inicO})_4(\text{OH})_2(\text{SO}_4)(\text{H}_2\text{O})_4]$.²⁴ The isonicotinato N-oxide ligand is bonded bidentately to the copper atom, chelating through both carboxylato oxygen atoms in $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$; whereas in $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$ it is bonded monodentately through one carboxylato oxygen atom, as in $[\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4]$.²²

3.3. Molecular Packing and Hydrogen Bonding

$[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ and $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ are polymeric complexes with chain structure, where the structural units are connected by nicotinato N-oxide bridges (Figs. 3 and 4).

In $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$ the trinuclear structural units are connected together by nicotinato N-oxide bridges, the N-oxide oxygen of the adjacent unit forming a bridge between the terminal and central copper atoms with a rather long Cu-O interaction (2.426(2) and 2.672(1) Å). Strong hydrogen bonds of 2.66-2.69 Å are formed between the N-oxide oxygen and the aqua ligands coordinated to the terminal copper atoms. The hydroxo bridge and the uncoordinated carboxylato oxygen are connected by a hydrogen bond (Table 12).

Double bridges formed by nicotinato N-oxide ligands join copper atoms to each other in $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$. The structural units are joined together through long Cu-O(N-oxide) distances (2.468(6), 2.577(6) Å), forming zig-zag chains packed into layers, between which there are layers of lattice water molecules. The aqua ligands are connected by probable hydrogen bonds to N-oxide oxygen atoms. Lattice water molecules form hydrogen bonds of 2.69-2.89 Å to each other. In addition, two of the four lattice water molecules are attached by hydrogen bonds of 2.70-2.81 Å to the uncoordinated carboxylato oxygen atoms.

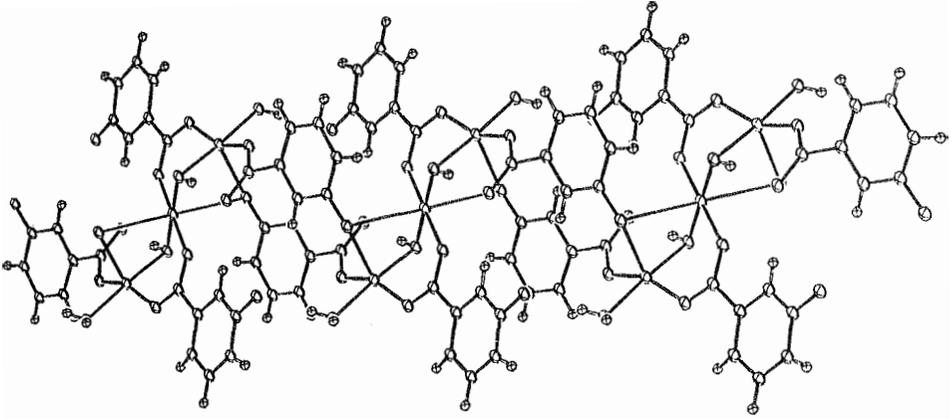


Fig. 3. Structure of polymeric $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$.

Table 12. Hydrogen bonds of $[\text{Cu}_3(\text{N-nicO})_4(\text{OH})_2(\text{H}_2\text{O})_2]$.

O-H...O'	Distance(Å)			Angle(°)
	O-H	H...O'	O---O'	
O(7)-H(9)...O(1)	0.76(3)	1.91(3)	2.660(2)	167(3)
O(7)-H(10)...O(1)	0.54(4)	2.16(4)	2.691(2)	171(4)
O(8)-H(11)...O(5)	0.40(4)	2.42(4)	2.789(3)	153(7)

$[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ slowly decomposes at room temperature releasing water. The very easy loss of the lattice water molecules indicates a lamellar structure and a bonding mode of water molecules. The loss of the water molecules in three successive steps can be seen in the thermogravimetric curve (Ref. 2, fig. 3). Probably the two waters bonded only to each other leave first, and then those bonded also to carboxylato oxygen atoms. The loss of the lattice water molecules is followed by the loss of the aqua ligands, beginning about 115 °C.

The complex molecules of $[\text{CuCl}_2(\text{N-nicOH})_2]$ are connected by hydrogen bonds of 2.690 Å between the carboxylic OH group and N-oxide oxygen atoms and a weak interaction between the copper(II) ion and a carboxylic oxygen atom of the adjacent molecule (Fig. 5).

Hydrogen bonds of 2.67-2.79 Å between aqua ligands bonded to the terminal copper atoms and N-oxide oxygen atoms join together the molecules of $[\text{Cu}_3(\text{N-inicO})_4(\text{OH})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}$. The aqua ligand coordinated to the central copper atom forms hydrogen bonds to two lattice waters. A six-membered ring is generated through an intramolecular hydrogen bond of 2.709(3) Å formed between the uncoordinated carboxylato oxygen atom and the μ -hydroxo ligand.

In $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$, hydrogen bonds between aqua ligands and N-oxide oxygen atoms hold molecules in the crystal lattice. The hydrogen bond angles (143(6), 133(6)°) are smaller than the ideal ones.

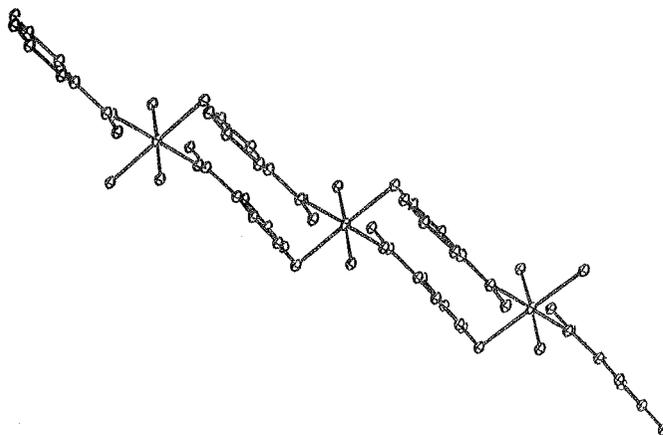


Fig. 4. View of the $[\text{Cu}(\text{N-nicO})_2(\text{H}_2\text{O})_2]$ chain.

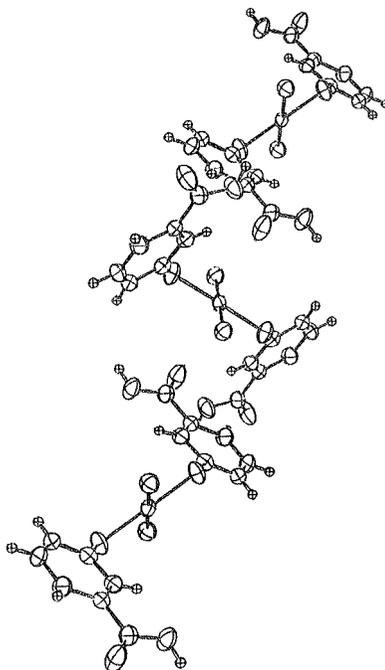


Fig. 5. Orientation of the $[\text{CuCl}_2(\text{N-nicOH})_2]$ molecules.

When pyridine molecules join to $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2]$ to give the new complex $[\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2(\text{py})_2]$, the long Cu-O(carboxylato) interaction is broken and an intramolecular hydrogen bond is generated between aqua ligands and uncoordinated carboxylato oxygen atoms. Molecules are held in the crystal lattice by hydrogen bonds of 2.782(1) Å between aqua ligands and N-oxide oxygen atoms.

In $[\text{Co}(\text{N-nicO})_2(\text{H}_2\text{O})_4]$, too, intramolecular hydrogen bonds are formed between aqua ligands and uncoordinated carboxylato oxygen atoms, and intermolecular hydrogen bonds connect the complex molecules to one other.

4. CONCLUSIONS

The central copper atom in the studied complexes has the coordination numbers four, five and six. The coordination geometries are square planar, square pyramidal and octahedral, respectively. These more or less distorted arrangements are normal for the copper atom. The coordination environments of the cobalt and nickel atoms are regular octahedron.

The potential coordinating groups, the carboxylate and N-oxide groups of nicotinic and isonicotinic acid N-oxide, compete for the coordination sites of the central metal atom. Being in meta- and para-position, respectively, in the pyridine ring, it is impossible for steric reasons for the groups to attach to the same central atom. The simultaneous attachment of the carboxylate and N-oxide groups in Cu(II) complexes of nicotinic acid N-oxide leads thus to polymeric structures with the ligands acting as bridges. Both nicotinic and isonicotinic acid N-oxide are able to form polynuclear complexes, the carboxylate group and the N-oxide oxygen atom acting as a bridge in complexes of nicotinic acid N-oxide and the carboxylate group in complexes of isonicotinic acid N-oxide.

The coordination mode of the nicotinate and isonicotinate N-oxide ligands varies from one complex to another. In the complexes prepared in aqueous solution

the N-oxide group seems to have a weaker ability to attach to the central metal atom than the carboxylate group. In the polymeric Cu(II) complexes of nicotinic acid N-oxide the N-oxide oxygen is coordinated to the copper atom by a rather weak interaction, which serves to join the structural units to each other. In the cobalt(II) and nickel(II) complexes the N-oxide group is not coordinated.

When ethanol is used as synthesis medium a significant change occurs in the coordination mode of nicotinic acid N-oxide and it is able to join to the central copper atom through the N-oxide oxygen alone, with a normal Cu-O bond distance.

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