

Synthesis and X-Ray Crystal Structure of Dichlorobis-(nicotinic acid *N*-oxide)copper(II)

HILKKA KNUUTTILA

Department of Chemistry, University of Jyväskylä, SF-40100 Jyväskylä 10, Finland

A new copper(II) complex of nicotinic acid *N*-oxide (*N*-nicOH), dichlorobis(nicotinic acid *N*-oxide)copper(II), $[\text{CuCl}_2(\text{N-nicOH})_2]$, has been prepared. The crystal and molecular structure has been determined by X-ray techniques and refined to a final *R*-value of 0.050.

The complex forms as one of the synthesis products of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and nicotinic acid *N*-oxide in ethanolic solution. The space group is $P2_1/c$, with $Z=2$ and cell dimensions are $a=6.019(4)$, $b=13.155(11)$, $c=10.418(8)$ Å and $\beta=115.80(5)^\circ$. Two chloride ligands are joined to the copper(II) ion, along with two nicotinic acid *N*-oxide ligands through the *N*-oxide oxygen atom in a distorted square planar arrangement. The coordination sphere of copper(II) ion is completed by two carboxylic oxygen atoms of adjacent molecules at very long distances [3.082(4)Å].

Several 3*d* metal complexes of nicotinic acid *N*-oxides have been synthesized from aqueous solution and characterized.¹⁻³ Recently, we determined the structures of two polymeric copper(II)^{4,5} and the isomorphous cobalt(II) and nickel(II)⁶ complexes of nicotinic acid *N*-oxide by X-ray diffraction analysis.

Metal complexes of monocarboxylic acid *N*-oxides have also been prepared in non-aqueous conditions. The magnetic moment of the complex of copper(II) chloride with pyridine *N*-oxide, tetrachlorobis- μ -(pyridine *N*-oxide)dycopper(II), was observed to be subnormal (0.85 B.M.).⁷ In the structure copper(II) ions are bridged by oxygen atoms of the pyridine *N*-oxides.⁸ Subnormal magnetic moments were also observed in dimeric complexes of copper(II) halides and

substituted pyridine *N*-oxide, including a copper(II) complex of nicotinic acid *N*-oxide.⁹ In ethanolic solution, prepared copper(II) halide complexes of pyridine *N*-oxides with an electron-withdrawing substituent such as COOH produce an even larger demagnetization than the parent Cu(II) complex with pyridine *N*-oxide.¹⁰

Low hydrates of 3*d* metal complexes with nicotinic and isonicotinic acid *N*-oxides have been prepared from *N,N*-dimethylformamide.¹¹ Copper(II) chloride¹² and 3*d* metal perchlorate¹³ adducts have been synthesized from ethanol-triethylorthoformate solution.

In this paper we present the structure of a new complex of copper(II) chloride and nicotinic acid *N*-oxide prepared from ethanolic solution.

EXPERIMENTAL

Preparation of the complex. Copper(II) chloride dihydrate (0.01 mol) dissolved with ethanol was added to a suspension of nicotinic acid *N*-oxide (0.01 mol) and ethanol. The mixture was refluxed for 2-3 h on a hot-plate. A few drops of 2 M HCl were added to the clear solution, which was then left to stand at room temperature. Two kinds of crystals separated from the solution: as the main product yellow needle-like crystals, too tiny for X-ray structure analysis, and after several months a few green crystals corresponding to the formula $\text{CuCl}_2(\text{N-nicOH})_2$, whose structure could be determined.

Data collection and structure determination. The crystal and refinement data are given in Table 1. The crystal and intensity data were measured on a Syntex $P2_1$ four-circle diffracto-

Table 1. Crystal and refinement data of $[\text{CuCl}_2(\text{N-nicOH})_2]$.

F. W.	412.67
Space group	$P2_1/c$
a (Å)	6.019(4)
b	13.155(11)
c	10.418(8)
β (°)	115.80(5)
Z	2
V (Å ³)	742.7
Collection mode	$\theta/2\theta$
Radiation	$\text{MoK}\alpha$ ($\lambda=0.71069$ Å)
Scan range	$4^\circ < 2\theta < 55^\circ$
Scan rate (°min ⁻¹)	1.0 → 15.0
Refl. meas.	2000
obs. ($I > 2.5\sigma(I)$)	1107
$F(000)$	410
$R = (\sum F_o - F_c) / \sum F_o $	0.050

meter using graphite monochromatized $\text{MoK}\alpha$ radiation. The unit cell parameters were calculated by least-squares refinement of 15 high order reflections.

Corrections were applied for Lorentz and polarization effects but not for absorption ($\mu = 19.2 \text{ cm}^{-1}$).

The structures were solved by direct methods (positions for copper and chlorine atoms) and

Fourier synthesis. Refinement was carried out by block diagonal matrix least-squares calculations with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for hydrogen atoms located by difference Fourier syntheses. The final R -value with unit weights was 0.050. The final atomic coordinates and the thermal parameters, $U_{\text{eq}} [= \frac{1}{3} \times (U_{11} + U_{22} + U_{33})]$, are given in Table 2. Lists of structure factors and anisotropic thermal parameters are available from the author upon request. Programs, computer and sources of scattering factor data are given in Ref. 14.

DISCUSSION

A drawing of the molecular structure is given in Fig. 1 and interatomic distances and angles are given in Table 3. The central copper(II) ion occupying the special position $(\frac{1}{2}, 0, 0)$ of the space group $P2_1/c$ is coordinated to two nicotinic acid N -oxide ligands monodentately through the N -oxide oxygen atom and to two chloride ligands in distorted square planar arrangement. Formally the coordination sphere of Cu(II) ion is completed by two oxygen atoms [0(3)] of the carboxylic groups of adjacent molecules. This $\text{Cu(1)}-0(3)$ distance, 3.082(4) Å, is rather long, 0.4 Å greater than the sum of the corresponding

Table 2. Final positional parameters and thermal parameters, $U_{\text{eq}} (\times 10^3)$ for non-hydrogen atoms and $U_{\text{iso}} (\times 10^2)$ (Å²) for hydrogen atoms.

Atom	x	y	z	U_{eq}
Cu(1)	0.5000	0.0000	0.0000	31.0(3)
Cl(1)	0.6979(2)	0.0720(1)	0.2153(1)	40.9(6)
O(1)	0.2841(5)	-0.0802(2)	0.0580(3)	41(2)
O(2)	0.9304(6)	-0.2855(2)	0.4053(3)	59(2)
O(3)	0.8281(6)	-0.3086(3)	0.5840(3)	62(2)
C(1)	0.5419(8)	-0.1640(3)	0.2665(4)	35(2)
C(2)	0.6021(7)	-0.1907(3)	0.4042(4)	34(2)
C(3)	0.4662(8)	-0.1507(3)	0.4708(4)	43(3)
C(4)	0.2818(8)	-0.0835(3)	0.3995(5)	44(2)
C(5)	0.2233(8)	-0.0584(3)	0.2612(5)	40(2)
C(6)	0.7986(8)	-0.2680(3)	0.4758(4)	42(2)
N(1)	0.3527(6)	-0.1003(3)	0.1974(3)	35(2)
				U_{iso}
H(1)	0.602(9)	-0.182(4)	0.200(5)	8(2)
H(2)	0.531(8)	-0.164(3)	0.568(4)	5(1)
H(3)	0.186(7)	-0.059(3)	0.441(4)	3(1)
H(4)	0.092(9)	-0.015(4)	0.195(5)	8(2)
H(5)	1.035(10)	-0.336(4)	0.451(5)	9(2)

Table 3. Selected bond distances (Å) and bond angles (°) with their standard deviations for [CuCl₂(*N*-nicOH)₂].

Environment of copper(II)			
Cu(1)–O(1)	1.962(3)	O(1)–Cu(1)–Cl(1)	86.92(8)
Cu(1)–Cl(1)	2.241(1)	Cl(1)–Cu(1)–O(1)	93.08(8)
Cu(1)–O(3)	3.082(4)	O(3)–Cu(1)–Cl(1)	93.74(6)
		O(3)–Cu(1)–Cl(1)	84.34(12)
Pyridine <i>N</i> -oxide group			
N(1)–O(1)	1.352(4)	Cu(1)–O(1)–N(1)	120.1(2)
N(1)–C(1)	1.343(5)	O(1)–N(1)–C(1)	119.2(4)
N(1)–C(5)	1.342(7)	O(1)–N(1)–C(5)	118.7(3)
C(1)–C(2)	1.365(6)	C(1)–N(1)–C(5)	122.1(4)
C(2)–C(3)	1.386(7)	N(1)–C(1)–C(2)	119.9(4)
C(3)–C(4)	1.359(6)	C(1)–C(2)–C(3)	119.0(4)
C(4)–C(5)	1.367(7)	C(2)–C(3)–C(4)	119.5(4)
		C(3)–C(4)–C(5)	120.6(5)
Carboxylic acid group			
C(6)–C(2)	1.490(6)	O(2)–C(6)–O(3)	124.9(4)
C(6)–O(2)	1.315(7)	O(2)–C(6)–C(2)	112.4(4)
C(6)–O(3)	1.190(6)	O(3)–C(6)–C(2)	122.6(5)
O(2)–H(5)	0.92(5)		

van der Waals radii, indicating a very weak interaction.

The angle between the coordination plane of the copper(II) ion and pyridine *N*-oxide group is 81.7°.

In the present complex, nicotinic acid *N*-oxide acts as monodentate ligand coordinating only through *N*-oxide oxygen. The Cu–O(*N*-oxide) bond length, 1.962(3) Å, is in good agreement with reported copper–oxygen(*N*-oxide) distan-

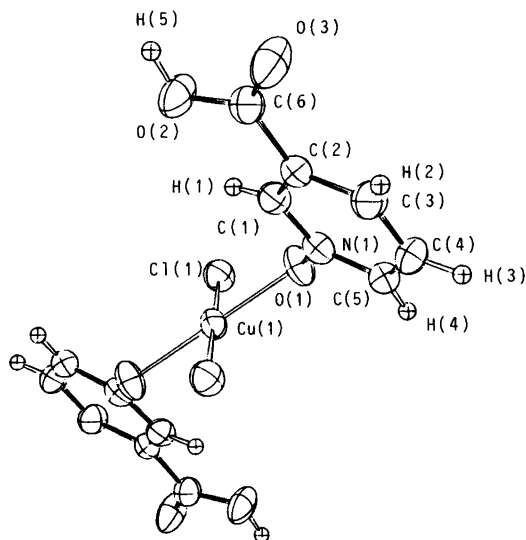


Fig. 1. The labelling and structure of [CuCl₂(*N*-nicOH)₂]. Thermal ellipsoids are drawn to enclose the 50 % probability level.

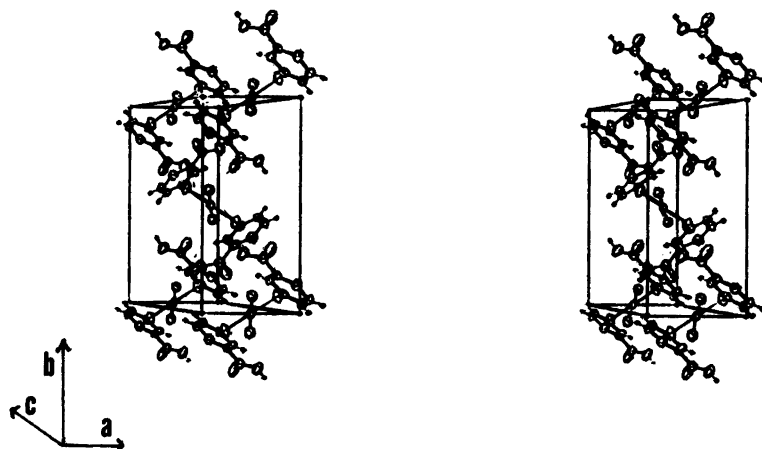


Fig. 2. Stereoview of the packing of $[\text{CuCl}_2(\text{N-nicOH})_2]$ within the unit cell.

ces:^{15-19,22} 1.97(1) and 1.93(1) Å in dichlorobis(2,6-lutidine *N*-oxide)copper(II), for instance.¹⁵

In the polymeric copper(II) complexes of nicotinic acid *N*-oxide prepared in aqueous solution, nicotinato *N*-oxide acts as a bidentate ligand coordinating either through both carboxylato oxygen atoms or through one carboxylato oxygen atom and the *N*-oxide oxygen to adjacent copper(II) ions. Polymerization occurs via a rather long Cu–O(*N*-oxide) interaction (2.43–2.67 Å).^{4,5,23} In the isomorphous cobalt(II) and nickel(II) complexes, tetraaquabis(nicotinato *N*-oxide)cobalt(II) and -nickel(II), nicotinato *N*-oxide joins monodentately through one carboxylato oxygen atom to the central metal ion.⁶

The Cu–Cl bond distance is 2.241(1) Å. Reported Cu–Cl distances for complexes of pyridine *N*-oxides¹⁵⁻²⁰ vary widely (2.206–2.955 Å) since the chlorine atom is sometimes coordinated to just one copper and sometimes acts as a bridging atom, in which case one of the Cu–Cl distances may be quite long.

In the carboxylic acid group the C–O distances are C(6)–O(2)(hydroxy) 1.315(7) and C(6)–O(3) 1.190(6) Å and in free nicotinic acid *N*-oxide 1.301(1) and 1.198(1) Å, respectively.²¹

Molecules are held in the crystal lattice by hydrogen bonds between *N*-oxide oxygens and carboxylic OH groups. Distances are O(2)–H(5) 0.915 Å, H(5)···O(1) 1.78(5) Å, O(2)–O(1)* 2.690(4) Å and the angle O(2)–H(5)–O(1) is 171 (5)°. The packing of the molecules is seen in Fig. 2.

* Symmetry operation: $x-1, -y-1/2, z-1/2$.

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