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The Structure of Polymeric Diaquo-di-μ-hydroxo-bis-μ-(nicotinato-N-oxide)-bis-μ-(nicotinato-N-oxido)tricopper(II)

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The new unusual polymeric copper(II) complex with nicotinate N-oxide (N-nicO), $[Cu_3(N\text{-}nicO)_4(OH)_2(H_2O)_2]_n$ *was prepared and its crystal and molecular structure was determined from three-dimensional X-ray diffraction data. The crystals belong to the triclinic space group* $P\bar{1}$ *(No. 2). The cell parameters are* $a = 7.881(9)$, $b = 9.658(11)$, $c = 10.368(12)$ Å, $\alpha = 97.32(9)$, $\beta = 110.38(9)$, $\gamma = 109.53(9)°$, $V = 670(1)$ Å^3, $d_{obs} = 1.94$ ($d_{calc} = 2.02$) *and* $Z = 1$. *The structure was refined to a final* R-*value of 4.13%.*

The complex is a polymeric, linear chain along the c-axis, and its structure units are connected with each other through two N-oxide oxygen atoms. There are three copper atoms (Cu1, Cu2, Cu2′) that are very close to each other in the structure unit, and the Cu–Cu distances are 3.035 Å. The coordination around the copper atom Cu1 is square planar and around the copper atoms Cu2 and Cu2′ it is square pyramidal with long axial coordination.

Nicotinate-N-oxide acts as a bridging ligand and is coordinated bidentately either through both carboxylate O atoms forming a bridge between Cu1 and Cu2 (Cu2′) or through one carboxylate O atom and the N-oxide O atom forming a double bridge between Cu2 and Cu2′ in separate structural units. Water molecules are coordinated with copper atoms Cu2 and Cu2′, and hydroxide groups form a bridge between Cu1 and Cu2, both Cu1 and Cu2′, respectively.

Introduction

Since 1961 considerable interest has been shown in metal complexes of the monocarboxylic acid N-oxides. Several complexes have been synthesized and reported [1–9]. In particular there have been studies on their spectral and magnetic behaviour, and on the basis of these properties some structures have been predicted. It has been proposed that nicotinic acid N-oxide acts as a bidentate bridging ligand coordinating through the N–O oxygen and the another carboxylic oxygen with dipositive 3d metal. Thus, linear, double bridged polynuclear species are formed.

The structures of the metal complexes of the substituted monocarboxylic acid N-oxides have been studied in our laboratory. While attempting the synthesis of complexes containing sulfate ion, two new copper nicotinato-N-oxide complexes, a triclinic and a monoclinic one corresponding the formulas $Cu_3(N\text{-}nicO)_4(OH)_2(H_2O)_2$ and $Cu(N\text{-}nicO)_2\cdot6H_2O$ were prepared. Repeated attempts to synthesize the previously reported $Cu(N\text{-}nicO)_2\cdot4H_2O$ [5] as single crystals yielded the same two copper complexes as above. The structures of both complexes have been determined and this paper deals with the structure of $[Cu_3(N\text{-}nicO)_4(OH)_2(H_2O)_2]_n$, in which there are three copper atoms close to each other in one structure unit. One Cu atom is tetracoordinated and two are pentacoordinated.

Experimental

The Preparation of the Crystals

In this experiment nicotinic acid N-oxide (99%, Aldrich-Europe) was used as received and the hydrated copper sulfate and NH_3(aq) (Merck) was of reagent grade. The new copper(II) complexes were prepared by methods employed for synthesizing metal complexes of N-picolinate-N-oxide and N-nicotinate-N-oxide [1, 5]. 0.05 mol N-nicOH was dissolved in water by adding NH_3(aq) dropwise, under stirring. The aqueous solution of ammonium nicotinate-N-oxide was then heated on a plate for 2–3 hours to eliminate excess of NH_3. 0.0125 mol $CuSO_4\cdot5H_2O$ was dissolved in water by warming. The hot aqueous solutions were allowed to react (total volume was 250 ml) on a hot plate, and precipitation began immediately. The reaction mixture was kept hot for 1–2 hours. The small dark bluish green crystals were separated from the hot supernatant by filtration, washed with warm water, dried in air and stored in desiccator. The complex was insoluble in water and most organic solvents. It was analyzed as

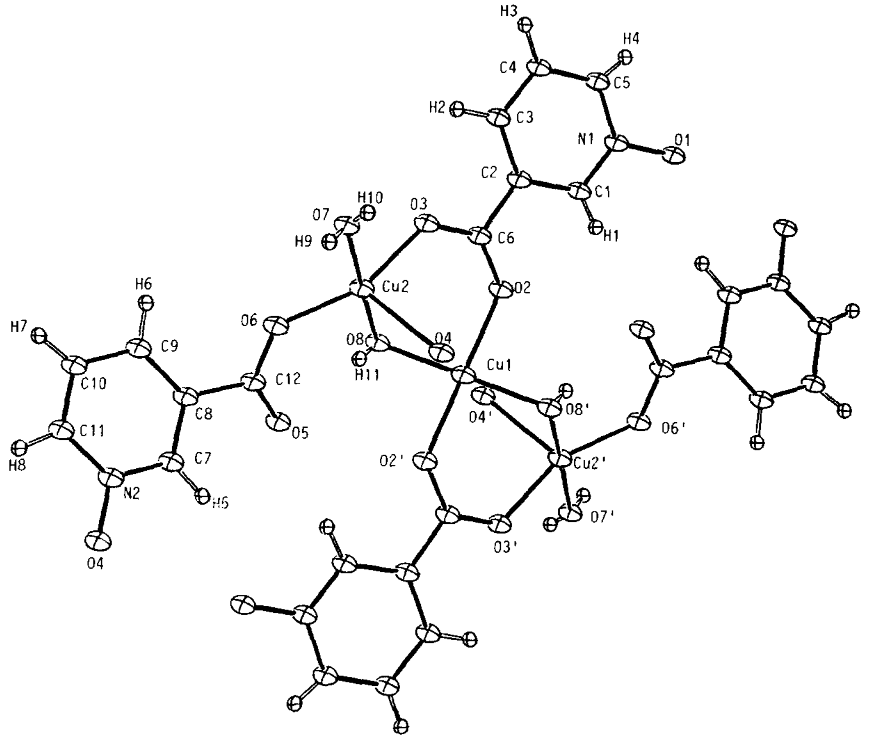

Fig. 1. An ORTEP drawing of one $Cu_3(N\text{-nicO})_4(OH)_2(H_2O)_2$ group including atomic labeling scheme.

TABLE I. Crystal Data for $[Cu_3(C_5H_4NOCOO)_4(OH)_2 \cdot (H_2O)_2]_n$.

a = 7.881(9) A		F.W.	= n·813.09
b = 9.658(11) A		d_{obs}	= 1.94 g cm^{-3}
c = 10.368(12) A		d_{calc}	= 2.01 g cm^{-3}
α = 97.32(9)°		Z	= 1
β = 110.38(9)°		$F(000)$	= 409
γ = 109.53(9)°			
V = 670(1) Å^3			
Space group: $P\bar{1}$ (No. 2)			

$Cu_3(N\text{-nicO})_4(OH)_2(H_2O)_2$. Copper was analyzed electrogravimetrically and C, H and N analyses were carried out in Central Laboratory, Helsinki, Finland.

Anal. Calcd. for $Cu_3(N\text{-nicO})_4(OH)_2(H_2O)_2$: Cu, 23.446%; C, 35.453%; N, 6.891%; H, 2.727%. Found: Cu, 23.28%; C, 35.19%; N, 6.87%; H, 2.76%. The density, d_{obs} = 1.94 g cm^{-3} (d_{calc} = 2.02 g cm^{-3}), was measured using the flotation technique.

The supernatant was allowed to cool, and then large light green crystal-like plates were separated. These crystals were analyzed as $Cu(N\text{-nicO})_2 \cdot 6H_2O$. The structure of this copper(II) complex has also been determined and the results will be reported later.

Data Collection

Both the crystal data, Table I, and the intensity data were measured on a Syntex $P2_1$, the automatic four-circle diffractometer employing graphite monochromatized MoKα-radiation for data collection. The unit cell parameters were calculated by least squares refinement of 15 reflections. The space group was triclinic $P\bar{1}$ (No. 2). The intensities of 3833 reflections were collected ($5 < 2\theta < 50°$) at room temperature using the $\theta/2\theta$-scan technique with the scan rate varying from 1.00 to 15.0° min^{-1} depending on the peak intensity. The intensity of one standard reflection, recorded after every 50 measurements to monitor the crystal stability, remained essentially constant throughout the data collection. Out of 3833 measured reflections 2525 were observed on the basis of $I > 3\delta(I)$. The data were corrected for Lorentz and polarisation factors but not for absorption.

Structure Determination

The solving and refinement of the structure was carried out by the X-Ray System programs [10], and a UNIVAC 1100/10 computer. The scattering factors for Cu, C, N and O were those of Cromer and Mann [11] and for hydrogen atoms those reported by Stewart *et al.* [12]. The anomalous dispersion corrections for copper were also included in calculations [13]. The molecule was supposed to be centro-

TABLE II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Non-hydrogen Atoms with Their Standard Deviations. The anisotropic thermal parameters are of 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}
CuI	0.00000	0.00000	0.00000	30.6(2)	25.3(1)	27.6(1)	11.5(1)	20.7(1)	14.1(1)
Cu2	0.05250(4)	0.26157(2)	0.22723(2)	32.2(1)	26.2(1)	24.6(1)	8.6(1)	19.2(1)	11.0(1)
O1	0.5940(2)	0.5923(2)	0.3634(1)	40.4(9)	41.0(7)	26.7(6)	19.8(6)	24.4(6)	11.1(6)
O2	0.8794(2)	0.8208(1)	0.0578(1)	40.2(8)	26.3(6)	33.5(7)	11.3(6)	27.1(6)	14.5(5)
O3	0.1445(2)	0.3725(1)	0.1001(1)	41.7(9)	28.6(6)	27.3(6)	8.2(6)	23.4(6)	11.9(5)
O4	0.2792(2)	0.1363(2)	0.2673(2)	42.4(9)	41.5(8)	46.2(8)	20.5(7)	29.5(7)	33.2(7)
O5	0.7453(3)	0.9726(2)	0.2747(2)	77(1)	32.0(7)	51.7(9)	6.7(8)	50(1)	8.0(7)
O6	0.9402(2)	0.2181(1)	0.3648(1)	42.9(9)	31.7(7)	31.0(7)	6.3(6)	26.4(6)	11.4(6)
O7	0.2480(2)	0.4432(1)	0.3775(1)	37.9(8)	32.4(7)	25.4(6)	8.2(6)	19.6(6)	11.6(5)
O8	0.8598(2)	0.0925(1)	0.0727(1)	27.6(7)	32.3(6)	22.3(6)	9.4(5)	13.7(5)	9.5(5)
N1	0.6396(2)	0.5368(2)	0.2624(1)	23.9(8)	30.9(8)	22.2(7)	7.5(6)	13.5(6)	12.9(6)
N2	0.2701(2)	0.0219(2)	0.3261(2)	23.5(8)	27.7(7)	29.5(7)	7.5(6)	14.8(6)	15.4(6)
C1	0.7183(3)	0.6316(2)	0.1939(2)	25(1)	26.9(8)	26.1(8)	6.8(7)	15.1(7)	12.5(7)
C2	0.7608(3)	0.5764(2)	0.0861(2)	22.2(9)	25.1(8)	21.5(8)	5.8(7)	11.9(7)	11.2(6)
C3	0.7252(3)	0.4255(2)	0.0488(2)	33(1)	30.4(9)	33.2(9)	15.2(8)	21.2(8)	14.5(8)
C4	0.6444(3)	0.3303(2)	0.1214(2)	36(1)	27.1(9)	44(1)	13.2(8)	23.3(9)	16.9(8)
C5	0.6021(3)	0.3885(2)	0.2269(2)	31(1)	33.1(9)	41(1)	10.8(8)	20.9(9)	24.9(8)
C6	0.8391(3)	0.6844(2)	0.0078(2)	22(1)	28.2(8)	24.4(8)	9.4(7)	14.3(7)	14.8(7)
C7	0.2413(3)	0.0265(2)	0.4469(2)	26(1)	33.6(9)	30.5(9)	12.6(8)	18.7(8)	15.2(7)
C8	0.7854(3)	0.0987(2)	0.4992(2)	24(1)	28.6(8)	25.5(8)	9.4(7)	14.8(7)	11.3(7)
C9	0.2250(3)	0.7755(2)	0.4341(2)	37(1)	31.5(9)	28.9(9)	15.0(8)	17.9(8)	16.4(8)
C10	0.2702(3)	0.7782(2)	0.3167(2)	43(1)	40(1)	29.3(9)	20.6(9)	20.7(9)	13.0(8)
C11	0.2912(3)	0.9024(2)	0.2643(2)	31(1)	45(1)	25.0(9)	16.5(9)	16.6(8)	15.7(8)
C12	0.8252(3)	0.0920(2)	0.3673(2)	33(1)	29.1(9)	28.3(8)	14.7(8)	20.6(8)	13.0(7)

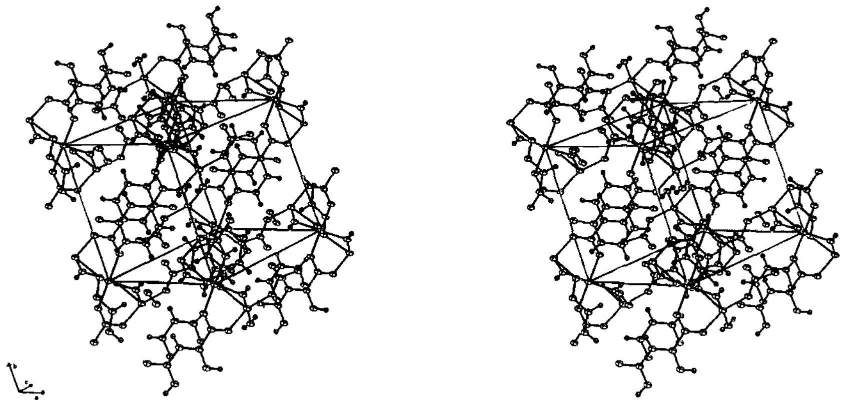

Fig. 2. A stereoview of the packing in the unit cell.

symmetric and one copper atom was located at origin. The other non-hydrogen atoms were located from the subsequent Fourier maps. Refinement of all non-hydrogen atoms with isotropic thermal parameters led to an *R*-value of 0.109. All hydrogen atoms were located from different Fourier maps. The final refinement of all non-hydrogen atoms with isotropic thermal parameters and the subsequent block-diagonal refinement with anisotropic temperature factors led to an *R*-value of 0.048. After the last two least squares cycles in which non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters, the final *R*-value was 0.0416. The final difference Fourier map showed no significant features.

Description of the Structure and Discussion

This new copper(II) complex of N-nicotinate-N-oxide, $[Cu_3(N\text{-}nicO)_4 \cdot (OH)_2(H_2O)_2]_n$ has the polymeric linear chain structure along the c-axis.

The structure of one unit of the polymer is shown in Fig. 1 and the packing in the unit cell in Fig. 2. the atomic coordinates and thermal parameters with their standard deviations for non-hydrogen atoms are given in Table II, and the coordinates of hydrogen atoms and isotropic thermal parameters in Table III. A table of the observed and calculated structure factors is available from the author. Intramolecular distances and angles with their standard deviations are shown in Table IV.

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

Atom	X	Y	Z	U
H1	0.732(4)	0.722(3)	0.221(2)	2.6(7)
H2	0.233(4)	0.609(3)	0.016(3)	4.5(8)
H3	0.609(4)	0.222(3)	0.088(2)	4.6(7)
H4	0.563(4)	0.347(3)	0.286(2)	3.9(7)
H5	0.226(3)	0.111(2)	0.483(2)	2.7(6)
H6	0.212(3)	0.686(2)	0.469(2)	2.2(4)
H7	0.296(4)	0.701(3)	0.276(2)	3.9(7)
H8	0.320(4)	0.917(3)	0.182(2)	3.7(7)
H9	0.277(4)	0.428(3)	0.451(3)	4.9(9)
H10	0.312(5)	0.471(4)	0.367(3)	8.3(12)
H11	0.861(5)	0.070(4)	0.103(3)	6.0(12)

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

Cu1–O2	1.954(1)	O6–C12	1.262(2)	O2–Cu1–O8	87.28(7)
Cu1–O8	1.912(2)	O5–C12	1.208(2)	O2′–Cu1–O8	92.72(7)
		C7–C8	1.379(3)		
Cu2–O3	1.979(2)	C8–C9	1.362(3)	O3–Cu2–O6	158.73(7)
Cu2–O4	2.426(2)	C8–C12	1.503(3)	O3–Cu2–O7	84.55(5)
Cu2–O6	1.943(2)	C9–C10	1.383(3)	O7–Cu2–O6	84.84(6)
Cu2–O7	1.925(1)	C10–C11	1.363(3)	O6–Cu2–O8	97.55(6)
Cu2–O8	1.876(1)	C11–N2	1.336(3)	O8–Cu2–O3	92.27(5)
		N2–O4	1.322(2)	O4–Cu2–O3	95.26(7)
O2–C6	1.240(2)			O4–Cu2–O6	103.56(7)
O3–C6	1.250(3)	C1–H1	0.840(26)	O4–Cu2–O7	92.37(6)
C1–C2	1.369(3)	C3–H2	0.921(34)	O4–Cu2–O8	89.84(6)
C2–C3	1.364(3)	C4–H3	0.968(24)	O7–Cu2–O7	176.28(6)
C2–C6	1.504(3)	C5–H4	0.866(29)		
C3–C4	1.391(3)	C7–H5	0.920(26)	Cu2–O6–C12	129.1(1)
C4–C5	1.359(4)	C9–H6	0.969(19)	O6–C12–O5	126.2(2)
C5–N1	1.336(3)	C10–H7	0.923(30)	O6–C12–C8	114.3(1)
N1–O1	1.327(3)	C11–H8	0.969(28)	O5–C12–C8	119.5(2)
		O7–H9	0.765(29)		
		O7–H10	0.536(40)	Cu2–O3–C6	126.4(1)
		O8–H11	0.401(38)	O3–C6–O2	127.2(2)
				O2–C6–C2	115.8(2)
				O3–C6–C2	116.9(2)
				H9–O7–H10	112(4)
				H11–O8–Cu2	84(3)
				H11–O8–Cu1	94(6)

In one structural unit of the polymer there are three copper atoms (Cu1, Cu2 and Cu2′) quite close to each other. The distance between them is 3.035 Å. Four nicotinate N-oxide groups, two hydroxide groups and two water molecules are coordinated with the copper atoms. The structural units are connected with each other through two N-oxide oxygen atoms which are coordinated to Cu2 and Cu2′ atoms in separate units. In this complex copper atoms are found to be both penta- and tetracoordinated. The coordination around Cu1 is square planar. The distance of the atoms from the least squares planes is given in Table V.

The nicotinate-N-oxide group forms a bridge between Cu1 and Cu2 (Cu2′), through both carboxylate oxygen atoms. The hydroxide group also acts as a bridge ligand between Cu1 and Cu2 (Cu2′). The distances between the copper atoms and the

TABLE V. The Distance of the Copper Atoms and the Coordinated Atoms from the Least Squares Plane.
Plane 1 = (Cu1, O2, O2', O8, O8')
Plane 2 = (Cu2, O3, O8, O7).

Plane	Equation of the plane	Atom	Distance (Å)
1	PX + QY + RZ = S	Cu1	0.00
	P = 3.3916	O2	0.00
	Q = 0.2447	O2'	−0.00
	R = 6.2294	O8	0.00
	S = 0.0000	O8'	−0.00
2	PX + QY + RZ = S	Cu2	−0.02
	P = −6.9703	O3	−0.00
	Q = 6.9613	O8	0.01
	R = 0.8671	O7	0.01
	S = 1.6732	O6	0.49

hydroxide oxygen atoms are Cu1–O8, 1.912 Å and Cu2(Cu2')–O8, 1.876 Å.

The coordination around Cu2 (Cu2') is disturbed square pyramidal. Two nicotinate-N-oxide groups in transposition are coordinated to the copper atom equatorially by a carboxylate oxygen atom. One of these N–nicO groups forms a bridge to Cu1 through the other carboxylate O atom, and the other N–nicO acts as a bridge between two separate structure units of the polymer through the N-oxide oxygen, which is coordinated to the Cu2 atom axially. This Cu2–O4 bond distance (2.426 Å) is remarkably longer than the equatorial Cu–O bond distances (1.876–1.979 Å). One of these equatorial oxygen atoms differs 0.49 Å from the least squares plane of the atoms Cu2, O3, O7, O8, Table V. One water molecule is coordinated to Cu2 (Cu2') equatorially, the Cu–O bond distance is 1.925 Å.

Thus, nicotinate-N-oxide acts as a bidentately bridging ligand forming a bridge structure in two ways; either between two nearby copper atoms (Cu1, Cu2 (Cu2')) through both carboxylate O atoms, or between the Cu2 atoms of separate structure units through one carboxylate O atom and the N-oxide O atom.

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