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The Preparation, IR Spectrum and Structure of the Di-μ_3-hydroxo-μ-sulphato-tetrakis-μ-(isonicotinato-N-oxide)tetraaqua-tetracopper(II)

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A very unusual new copper(II) complex with isonicotinate N-oxide (N-inicO), $Cu_4(N\text{-}inicO)_4SO_4(OH)_2(H_2O)_4$ has been prepared and its crystal and molecular structure determined from three dimensional X-ray diffraction data. The crystals belong to the monoclinic space group C2. The cell parameters are a = *19.809(8),* b = *6.844(3),* c = *19.533(12) Å, β = 140.9(3)°, d_{obs} = 1.99, d_{calc} = 2.01 and Z = 2. The structure was refined to a final R-value of 0.062.*

The monomeric tetranuclear complex resembles a space ship with the sulphate group at its top and pyridine rings as wings. Two copper atoms are very close to each other in the molecule; the Cu1–Cu1′ distance is 2.855 Å. The coordination around all copper atoms is square pyramidal with a rather long axial coordination. Isonicotinate-N-oxide acts as a bridging ligand coordinating bidentately through both carboxylate O atoms and forming bridges between copper atoms Cu1 and Cu2. The N-oxide O atoms form hydrogen bonds with coordinated water molecules. Hydroxo groups form two three-fold bridges symmetrically between copper atoms Cu1, Cu1′, and Cu2, and the sulphate group forms a bridge between two copper atoms Cu1 and Cu1′. The sulphur of the sulphate group is situated at the special point of the space group.

Introduction

We have studied structures and coordination of the carboxyl and N-oxide groups in the metal complexes of monocarboxylic acid N-oxides by using the X-ray technique in our laboratory [1, 2] Up to now only their spectral and magnetic properties have been studied [3].

Another aim of this work was to study the coordination of the sulphate group. It can coordinate in four ways: acting as a monodentate [4–6], a bridging bidentate [7], a bridging tridentate [8, 8a] and a chelating ligand [9]. Several papers have reported on tetranuclear Cu(II) complexes. The structures with a M_4O_4-core are rather frequent [10–12], as well as some tetranuclear Cu(II) compounds with a μ_4-oxo group [13, 14]. Dimeric tetranuclear copper structures also exist [15, 16]. The copper(II)isonicotinato-N-oxide sulphato complex under study has a new core type structure (Cu_2O_4S) in which all four copper atoms are situated almost on the plane.

Experimental

Preparation of the Compound

The first step was to dissolve 0.03 mol of isonicotinic acid N-oxide in about 100 ml of hot water by adding NH_3(aq) dropwise. After dissolving the solution was kept hot for a few hours in order to remove the excess NH_3. The hot solution containing 0.03 mol of $CuSO_4 \cdot 5H_2O$ in 100 ml of water and the solution of the ammonium isonicotinate were then combined and filtered. After this about two grams of NaAc was added in the hot solution to raise the pH, immediately causing precipitation. On closer inspection of the precipitate two different kinds of crystals could be seen: green and blue. When the precipitate was filtered off the chemical balance favored the precipitation of the green crystals, analyzed as $Cu_4(N\text{-}inicO)_4SO_4(OH)_2(H_2O)_4$. The blue one was analyzed as $Cu(N\text{-}inicO)_2(H_2O)_2$, and its structure will be published later.

Cu was analyzed by standard EDTA titrations. The chemical analysis for C, N and H was performed by the Pulp and Paper Research Institute, in Espoo, Finland.

Analytical results: Cu% 25.20_{calc}, 24.53_{obs}; S% 3.18_{calc}; O% 34.89_{calc}; C% 28.58_{calc}, 28.24_{obs}; N% 5.55_{calc}, 5.54_{obs}; H% 2.60_{calc}, 2.62_{obs}.

IR spectra were recorded on a Perkin-Elmer 283 Infrared Spectrophotometer. The samples were run as KBr discs in the range of 4000–200 cm^{-1}.

Data Collection

The intensity data were measured on a Syntex $P2_1$ automatic four-circle diffractometer employing graphite monochromatized MoK_α-radiation. The unit cell parameters were calculated by least squares refinement of 15 high order reflections. There were three possible space groups: C2/m, Cm and C2; the

TABLE I. Some Infrared Absorption Bands (cm^{-1}).

$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	Coordinated water			μ_3-Bridging hydroxo bending	Sulphato			$\nu(NO)$	$\delta(NO)$
		$\nu(OH)$	$\delta(H-O-H)$	wagging, rocking stretching		ν_1, ν_3	ν_4	ν_2		
1625	1410	3300, 3100	1610	600–900	~1050	1000-1200	600-900	~450	1222	865

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 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}
Cu1	0.0750(2)	0.2226	0.0036(2)	19.0(9)	30(1)	18.8(8)	1(1)	14.2(7)	0(1)
Cu2	0.1813(2)	0.2998(5)	1.2420(2)	15.3(9)	24(1)	18.2(8)	−3(1)	13.3(7)	−3(1)
S1	0.0000	−0.3409(11)	1.0000	29(4)	14(3)	40(4)	0	23(3)	0
O1	0.0798(10)	0.1589(23)	0.1057(9)	21(6)	45(9)	21(6)	5(6)	17(5)	0(6)
O2	0.9286(10)	0.2088(36)	0.0975(10)	26(7)	106(15)	22(6)	−18(10)	19(6)	−11(9)
O3	0.0920(10)	0.3084(30)	0.2539(10)	23(6)	51(10)	30(6)	−13(8)	22(5)	−13(8)
O4	0.8687(11)	0.2798(27)	0.3643(10)	35(7)	32(9)	38(7)	−10(7)	32(6)	−8(7)
O5	0.2278(10)	0.2125(34)	0.1094(10)	19(6)	92(13)	23(6)	8(9)	14(5)	−6(9)
O6	0.2974(9)	0.3072(29)	0.2650(10)	22(6)	49(9)	29(6)	−6(8)	23(5)	−7(8)
O7	0.2050(9)	0.7711(26)	0.3992(10)	20(6)	37(11)	33(6)	−2(7)	19(5)	−9(7)
O8	0.5691(17)	0.0105(59)	0.0089(20)	36(11)	284(40)	90(15)	−19(20)	54(12)	20(23)
O9	0.5661(15)	0.2925(40)	0.0954(12)	76(12)	57(13)	34(8)	2(14)	24(8)	4(11)
O10	0.2677(11)	0.0602(24)	0.3577(10)	38(8)	32(8)	30(6)	11(7)	26(6)	8(6)
O11	0.2663(11)	0.5100(22)	0.3535(11)	33(8)	24(8)	36(7)	−3(6)	28(6)	−3(6)
C1	0.8239(15)	0.2542(37)	0.2140(14)	35(10)	26(16)	23(8)	2(10)	21(8)	1(8)
C2	0.3551(15)	0.7479(40)	0.1723(14)	28(9)	39(16)	27(8)	4(10)	21(8)	3(9)
C3	0.9631(13)	0.2667(34)	0.2382(12)	17(7)	34(17)	16(6)	−2(8)	14(6)	−1(8)
C4	0.0380(14)	0.2819(36)	0.3518(12)	26(8)	21(11)	24(7)	−6(9)	20(7)	−0(8)
C5	0.5035(14)	0.7869(37)	0.3905(12)	27(9)	20(9)	23(7)	−1(10)	19(7)	−0(9)
C6	0.4985(15)	0.7644(41)	0.1950(14)	33(10)	41(20)	26(8)	1(11)	25(8)	−1(10)
C7	0.6036(13)	0.2837(35)	0.4170(11)	22(8)	25(10)	17(6)	−9(9)	15(6)	−2(8)
C8	0.5047(13)	0.2846(36)	0.3723(13)	15(7)	23(10)	24(7)	1(9)	14(6)	−6(9)
C9	0.4112(13)	0.2707(37)	0.2579(12)	12(7)	38(17)	19(6)	2(9)	9(6)	2(8)
C10	0.9208(14)	0.7564(41)	0.1966(14)	23(9)	46(20)	27(8)	4(10)	19(7)	0(10)
C11	0.5204(14)	0.2577(42)	0.2424(14)	23(9)	42(20)	25(8)	2(10)	16(7)	−3(10)
C12	0.8019(14)	0.7645(46)	0.2074(14)	18(8)	55(22)	24(8)	−9(11)	12(7)	−10(11)
N1	0.3973(12)	0.7757(30)	0.3227(11)	32(8)	31(11)	29(7)	2(8)	27(7)	2(8)
N2	0.1093(11)	0.7709(24)	0.3535(11)	18(6)	14(10)	27(6)	−2(6)	18(6)	−5(6)

suitable refinement showed the right one to be C2. The intensities of 2956 reflections were collected ($5 < 2\theta < 75°$) 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. Out of 2956 measured reflections 1546 were observed on the basis of $I > 3\sigma(I)$. The data were corrected for Lorentz and polarisation factors but not for absorption ($\mu_{MoK_\alpha} = 27.8$ cm^{-1}).

Structure Determination

The structure was solved by the MULTAN 78 direct methods [17]. The location and refinement by th X-Ray System programs [18] of all non-hydrogen atoms with isotropic temperature parameters led to an R-value of 0.088. The scattering factors for Cu, S, O, C and N were those of Cromer and Mann [19] and for hydrogen atoms those reported by Stewart *et al.* [20]. The anomalous dispersion corrections for copper were also included in the calculations [21].

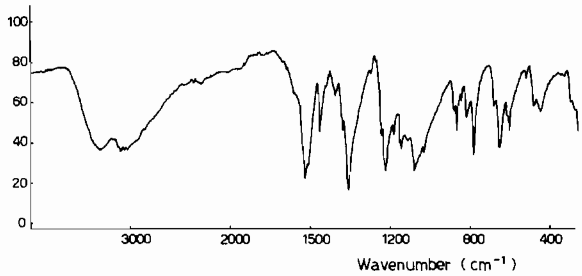


Fig. 1. Infrared spectra of KBr pellets of Cu_4(N-inicO)$_4$-$(OH)_2SO_4(H_2O)_4$.

The difference Fourier map showed two peaks (3.7 and 3.2 eÅ^{-3}) without a chemical meaning, very close to the copper atoms (0.5 Å). For this reason no attempt was made to locate the hydrogen atoms from the difference Fourier map. The final refinement of all non-hydrogen atoms with anisotropic temperature factors led to a final R-value of 0.062.

Results and Description of the Structure

Infrared Spectra

Table I lists the absorptions due to coordinated H_2O, COO, NO and SO_4. Figure 1 illustrates the IR data curve for Cu_4(N-inicO)$_4SO_4(OH)_2(H_2O)_4$.

The carboxylate group showed antisymmetric and symmetric stretching bands at 1625 and 1410 cm^{-1}. Coordinated water had two strong absorption bands in the regions 3300 and 3100 cm^{-1}. The H–O–H bending motion occurred in the range of 1610 cm^{-1} with $(COO)_{asym}$ absorption. The N–O stretching

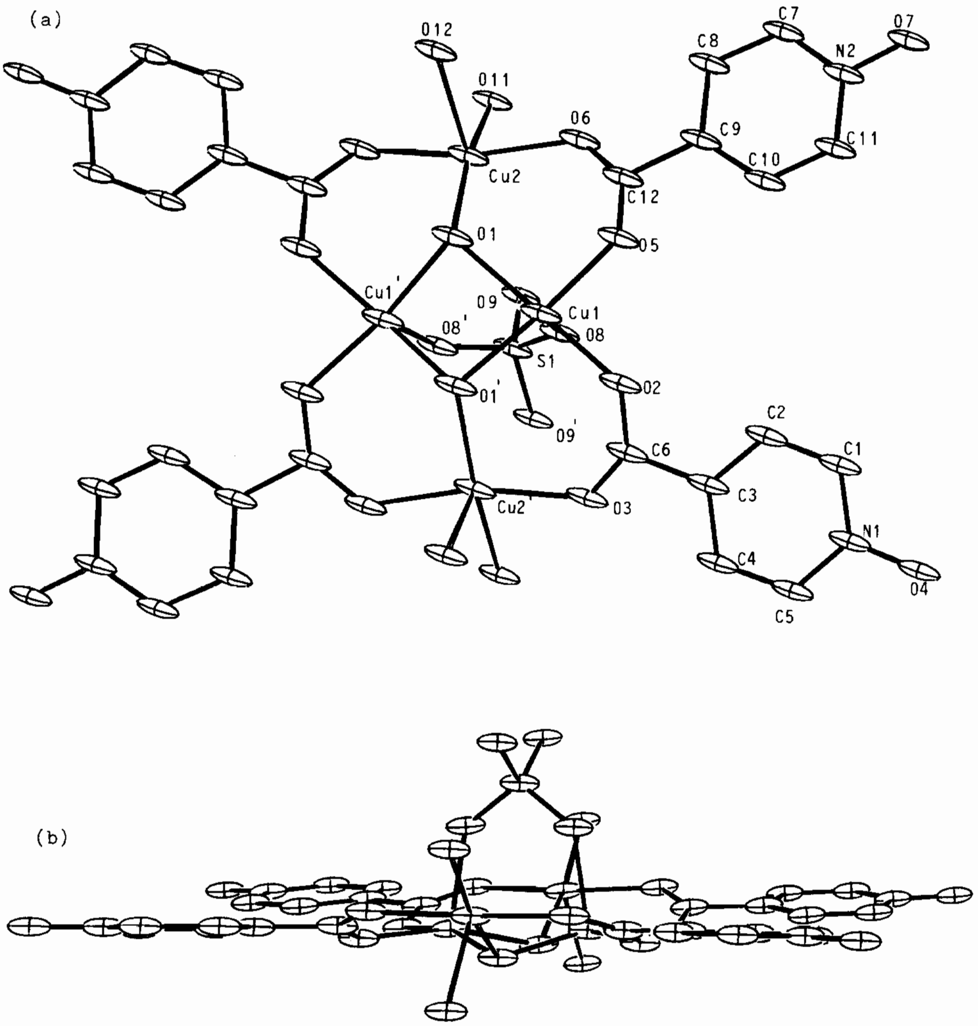


Fig. 2. An ORTEP drawing of Cu_4(N-inicO)$_4(OH)_2SO_4(H_2O)_4$ including atomic labeling scheme (a). The molecule has been rotated 90° about x-axes (b).

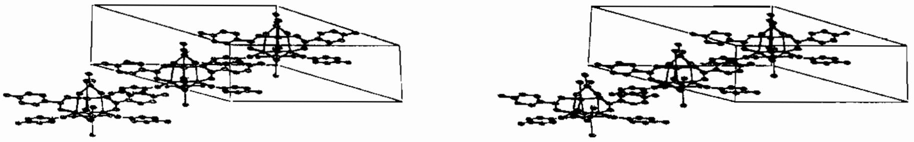


Fig. 3. A stereoview of the partial packing in the unit cell.

absorption band was at 1222 cm^{-1}. The band is broad, indicating hydrogen bonds. The T_d-symmetry of the sulphate group is reduced due to coordination to the C_{2v}, so that very strong ν_3 absorption bands of sulphate cannot be seen in the spectra. The ν_1 and ν_3 absorption bands of the sulphato group appear in the region 1200–1000 cm^{-1}. In the same region some absorptions of isonicotinate-N-oxide and the bridging OH groups also appear. The bands close to 1050 cm^{-1} may be due to the bridging OH bending mode.

The wagging, rocking and metal–oxygen stretching modes of coordinated water were seen in the regions 600–900 together with ν_4-absorptions of sulphato. These bands are very sensitive to the strength of the coordinate bond as well as to the hydrogen bonds in the crystals. N–O bending appears at 865 cm^{-1}, and ν_2 absorption of sulphato is at about 450 cm^{-1}.

The Structure Description

The atomic coordinates and thermal parameters with their standard deviations for non-hydrogen atoms are given in Table II. The labelling of the atoms in the molecule is shown in Fig. 2 and the partial packing in the unit cell can be seen in Fig. 3. Interatomic distances and angles with estimated standard deviations are given in Table III. In the structure of $Cu_4(N\text{-inicO})_4SO_4(OH)_2(H_2O)_4$ there are four pentacoordinated copper atoms which are connected together by four bridging carboxylic groups of N-inicO, by two μ_3-hydroxide groups, and by one bridged bidentate sulphate group. In the center of the structure the Cu_2O_4S cage can be seen.

TABLE III. Some Selected Interatomic Distances (Å) and Angles (°), with Their Standard Deviations.

Cu1–Cu1′	2.855(6)	Cu1–O1–Cu1′	92.1(5)
Cu1–O1	1.97(2)	Cu1–O1–Cu2	117.9(9)
Cu1–O1′	1.99(1)	O1–Cu1–O1′	82.4(7)
Cu1–O2	1.92(2)	O1′–Cu1–O5	165.2(8)
Cu1–O5	1.92(1)	O1–Cu1–O2	164.4(9)
Cu1–O8	1.92(4)	O1–Cu1–O8	97.3(14)
		O1–Cu2–O11	163.5(6)
Cu2–O1	1.95(1)	O3–Cu2–O6	166.9(5)
Cu2–O3	1.95(2)	O6–Cu2–O10	86.9(8)
Cu2–O6	1.96(2)	O6–C12–O5	129.3(25)
Cu2–O10	2.17(1)	O2–C6–O3	125.0(33)
Cu2–O11	1.99(1)	O8–S1–O8′	98.5(21)
		O8–S1–O9	114.8(13)
S1–O8	1.65(4)	O9–S1–O9	114.5(13)
S1–O9	1.50(2)		
Isonicotinate N-oxide Ligands			
O2–C6	1.26(2)	C10–C11	1.39(4)
O3–C6	1.24(3)	C7–N2	1.33(4)
C6–C3	1.46(5)	C11–N2	1.37(2)
C3–C2	1.40(3)	N2–O7	1.32(3)
C3–C4	1.42(3)		
C2–C1	1.35(5)		
C4–C5	1.36(5)		
C1–N1	1.37(3)		
C5–N1	1.36(3)		
N1–O4	1.30(4)		
O5–C12	1.26(2)		
O6–C12	1.24(4)		
C12–C9	1.53(4)		
C9–C8	1.42(2)		
C9–C10	1.35(5)		
C8–C7	1.39(3)		

The Coordination of the Copper Atoms

All copper atoms have a square pyramidal coordination surrounding. Cu1 coordinates with isonicotinate N-oxide through carboxyl oxygens O2 and O5, and with the μ_3-bridging hydroxo oxygen on the basal plane. Bonding distances are 1.92–1.99 Å. These values compare well with the corresponding Cu–O distances in the bis-[di-μ-(phenylmethoxo)-bis(pentane-2,4-dinato)dicopper(II)] (CuPhmP) [12]. The axial Cu1–O8 distance is 1.98 Å, which deviates from the axial Cu–O distance values of 2.42, 2.71 Å in CuPhmP [12] and of 2.15 Å in μ_3-hydroxo-tri-μ-(pyridine-2-carbaldehyde oximato)-μ_3-sulphato-tri-copper(II)-16.3-water (CuPCAO) [8a, 8]. Cu1 is clearly removed from the least-squares basal plane (O1′, O1, O5 and O2) towards the bridging sulphato group; the deviation is 0.27 Å. Cu2 has μ_3-oxygen O1, the carboxylate oxygens O6 and O3 and one water oxygen O11 in its basal coordination circle. The bonding distances are 1.94–1.99 Å and they correspond to the Cu1–O distances in its basal plane.

The apical distance Cu2–O10 is 2.17 Å and agrees with the previous value in CuPCAO, 2.15 Å [8, 8a]. Cu2 is situated on the plane with O1, O6, O11 and O3. The standard deviation of the atoms forming this plane is 0.12 Å.

TABLE IV. The Hydrogen Bonds.

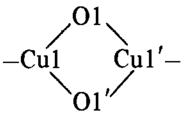
		Symmetry code
O4···O10	2.69(3) Å	*
O4···O11	2.63(3)	**
O7···O10	2.76(3)	***
O7···O11	2.67(3)	
O1···O9	2.51(3)	**

*x + ½, y + ½, z. **x + ½, y − ½, z. ***x, 1 + y, z.

The Coordination of the μ_3-OH Group

There have been descriptions in the literature of many compounds with the μ_3-OH or M_3O-core when the central metal is Fe(III), Cr(III) and Mn(III) [22–26], but only two systems that have Cu_3O-core [8, 8a, 27].

In this particular case two μ_3-OH link the other atoms together in both halves in the molecule. The copper–hydroxo–oxygen bonding distances are 1.94–1.99 Å and the angle Cu1–O1–Cu1′ is 92.2° and Cu2–O1–Cu1 is 117.1°. In the μ_3-hydroxo-(oxo)-tri-μ-(2-propylamino-2-methyl-3-butanone oximato)-triaqua-tricopper(II) (CuPrAO) [27] the Cu1–O1–Cu1′ angle is 110.9° and in the CuPCAO [8a, 8] the same angle is 108.2°, with Cu–O distances of 1.97 and 1.99 Å respectively. In the centre of the molecule there is a four-membered ring. The angles, O1′–Cu1–O1 and Cu1′–O1–Cu1 are 82.3° and 92.2° respectively. The ring is folded so that O1 is 0.53 Å under the least-squares plane of Cu1, O5 and O2. The Cu1–Cu1′ distance of 2.86 Å is quite short but is not the shortest possible. There are many Cu(II) compounds with a short metal–metal distance *e.g.* [1, 15, 28–31].



The Coordination of the Sulphate Group

The sulphur of the sulphate group is situated at the special point on the twofold axes. The sulphate acts as a bidentate bridge between Cu1 and Cu1′. The Cu–O distance to the sulphate oxygen O8 is 1.98 Å; this is a little shorter than the 2.15 Å in the CuPCAO complex [8, 8a]. The other oxygens O9 and O9′ of the sulphate group form intermolecular hydrogen bonds to the μ_3-hydroxo-oxygens O1 and O1′ of the second molecule. Data for the hydrogen bonds are given in Table IV.

The Coordination of the Isonicotinate N-oxide

The isonicotinate N-oxide acts as a bridging ligand. It coordinates with Cu1 and Cu2 via both of its carboxylic oxygens. The Cu–O bonding distances are from 1.92 to 1.97 Å. The N-oxide does not coordinate with Cu atoms but takes part in the intermolecular hydrogen bonds to the coordinated water molecules (O10 and O11).

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