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Catena-diaquabis-μ-(nicotinato-N-oxido)copper(II) Tetrahydrate: Structural, Thermogravimetric and IR Properties

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An unstable copper(II) complex with nicotinic acid N-oxide $\{[Cu(N\text{-}nicO)_2(H_2O)_2]\cdot 4H_2O\}_n$ *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* $P2_1$. *The cell parameters are* $a = 4.84(1)$, $b = 27.55(7)$, $c = 6.77(1)$ Å, $\beta = 106.08(17)^\circ$, $D_o = 1.79$, $D_c = 1.72$ *Mg* m^{-3} *and* $Z = 2$. *The structure was refined to a final* R*-value of 0.087.*

The copper complex is polymeric. Nicotinato N-oxido ligands are bonded bidentately through one carboxylato oxygen and the N-oxido oxygen atom, forming a double bridge between adjacent copper atoms. The central copper atoms have elongated octahedral geometry, such that the axial copper–N-oxido oxygen distances (2.577(6) and 2.468(6) Å) are longer than the equatorial copper–oxygen distances (average value 1.937 Å).

The decomposition of the complex has been followed thermogravimetrically and IR spectra of intermediates have been run. Lattice water begins to be released at room temperature and at about 83 °C only aqua ligands are left. The final fast decomposition of the complex begins at about 250 °C.

Introduction

Many metal complexes of pyridine monocarboxylic acid N-oxides have been synthesized in the last twenty-five years [1–10].

Karyannis *et al.* [5] have reported two Cu(II) complexes of nicotinic acid N-oxides, $Cu(N\text{-}nicO)_2\cdot 4H_2O$ and $Cu(N\text{-}nicO)_2\cdot 3H_2O$.

The structure determination of the present new copper(II) complex with nicotinic acid N-oxide forms part of the study of transition metal complexes of pyridine monocarboxylic acid N-oxides being undertaken in our laboratory. The aim of the study is to prepare new crystalline complexes of pyridine monocarboxylic acid N-oxides, to solve their structures, and to study coordination. The structures of the following complexes have been reported: polymeric diaquadi-μ-hydroxo-bis-μ-(nicotinato N-oxide)bis-μ-(nicotinato N-oxido)tricopper(II) [11], hexaaquacobalt(II) isonicotinate N-oxide, hexaaquanickel(II) isonicotinate N-oxide [12], and tetraaquadi-μ_3-hydroxo-μ-sulphato-tetrakis-μ(isonicotinato N-oxide) tetracopper(II) [13]. Nicotinic acid N-oxide acts as a bidentate ligand forming a bridge between adjacent copper(II) ions either through both carboxylato oxygen atoms or through one carboxylato oxygen and the N-oxido oxygen atom; isonicotinic acid N-oxide acts either as a mono- or bidentate ligand, coordinating through one or both carboxylato oxygen atoms, or as an anion.

Experimental

Preparation of the Complex

The copper(II) complex was prepared through a modification of the procedure employed for synthesizing the metal complexes of pyridine monocarboxylic acid N-oxides [1, 5, 11].

Nicotinic acid N-oxide (0.050 mol) was dissolved in water by adding dropwise $NH_3(aq)$, and by warming and stirring. Excess of NH_3 was eliminated by heating the aqueous solution for 2–3 hours. Water at room temperature and $CuSO_4\cdot 5H_2O$ (0.0125 mol) dissolved in water were added. From the cool reaction mixture light green crystal plates of the title compound were precipitated as the only product. The precipitation was left to stand overnight, after which it was filtered, washed with water and dried in air for 2–3 hours.

When the hot ammonium nicotinate N-oxide and aqueous $CuSO_4$ solutions were allowed to react on a hot plate for 2–3 hours, polymeric diaquadi-μ-hydroxobis-μ-(nicotinato N-oxide)bis-μ-(nicotinato N-oxido)tricopper(II) was precipitated in addition to the light green Cu(II) complex [11].

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TABLE I. Crystal Data.

Unit cell	*a* = 4.84(1) A
	b = 27.55(7) A
	c = 6.77(1) A
	β = 106.08(17)°
	V = 866(3) $Å^3$
Space group	$P2_1$
Z	2
D_{obs}	1.79 Mg m^{-3}
D_{calc}	1.72 Mg m^{-3}
F(000)	462
R	0.087
$\mu(MoK_\alpha)$	13.8 cm^{-1}
F.W.	nm 447.84

Physical Methods

Copper was analyzed electrogravimetrically and by standard EDTA titrations. *Anal.* for $[Cu(N\text{-}nicO)_2]\cdot4H_2O$: Cu% 14.19 (calc.), 14.26 (found).

Density was measured by a flotation technique. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer. The samples were run as KBr discs in the range 4000–200 cm^{-1}.

Thermogravimetric curves were run on a Fisher 100 TGA system equipped with a Multicorder model MC 611-3H recorder (Watanabe Instruments Co.). The heating rates were 2.5 °C/min.

Data Collection

Crystal data (Table I) and intensity data were measured on a Syntex $P2_1$ automatic four-circle diffractometer, employing graphite monochromatized MoK_α-radiation for data collection. The unit cell parameters were calculated by least-squares refinement of 15 reflections. The space group was monoclinic $P2_1$ (No. 4). After centering the crystal was coated with glue to prevent decomposition by loss of water. The intensities of 3433 reflections were collected ($4.0° < 2\theta < 70.0$) at room temperature using the ω-scan technique with the scan rate varying from 4.0 to 29.3° min^{-1} depending on the peak intensity. Out of 3433 reflections, 1355 were observed on the basis of $I > 3\sigma(I)$. The intensity of one standard reflection was recorded after every 100 measure-

TABLE II. Fractional Atomic Coordinates and Anisotropic Thermal Parameters ($\times10^2$) for Nonhydrogen Atoms with their Standard Deviations. The Anisotropic Parameters are of Form $\exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2C^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*b^*U_{13} + 2klb^*c^*U_{23}))$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.2466(4)	0.6528(1)	0.2588(2)	2.40(3)	3.65(3)	2.28(3)	0.14(4)	–0.50(2)	0.18(4)
O(1)	–0.4466(11)	0.1957(8)	0.0110(8)	2.4(3)	6.0(4)	4.0(3)	–0.9(3)	–2.4(3)	–0.4(3)
O(2)	0.4889(11)	0.1900(1)	0.5304(7)	2.6(3)	4.6(3)	2.4(3)	0.1(2)	–2.3(2)	0.0(2)
O(3)	0.6400(12)	0.2668(2)	0.5950(8)	3.8(3)	4.3(3)	5.3(3)	–0.8(3)	–2.7(3)	0.0(3)
O(4)	1.9370(10)	0.1124(2)	1.4777(7)	2.3(2)	3.6(3)	3.2(3)	–0.1(2)	–1.8(2)	–0.6(2)
O(5)	1.0295(10)	0.1195(2)	0.9670(7)	2.6(2)	2.2(2)	2.7(2)	0.2(2)	–1.8(2)	0.5(2)
O(6)	0.8875(11)	0.0422(2)	0.9087(7)	3.4(3)	2.8(3)	3.6(3)	–0.3(2)	–2.0(2)	–0.1(2)
O(7)	0.4757(10)	0.1043(2)	0.7122(7)	2.3(2)	4.1(3)	3.0(2)	0.3(2)	–0.7(2)	1.2(2)
O(8)	1.0338(11)	0.2078(2)	0.7834(7)	3.5(3)	5.9(3)	2.9(3)	–1.5(3)	–1.5(2)	0.4(2)
O(9)	0.7090(14)	0.8784(2)	0.1355(9)	5.6(4)	7.4(4)	5.8(4)	–0.9(4)	–0.1(3)	1.0(3)
O(10)	0.2218(16)	0.4469(3)	0.1708(9)	9.1(5)	7.2(4)	5.1(4)	1.9(4)	0.2(4)	–0.5(3)
O(11)	0.8192(15)	0.4293(2)	0.3683(9)	6.6(4)	7.7(5)	5.5(4)	–1.8(4)	0.8(4)	0.6(3)
O(12)	0.2821(12)	0.8637(2)	0.3423(8)	6.4(3)	3.6(3)	3.8(3)	1.2(3)	0.5(3)	0.9(2)
N(1)	–0.2528(12)	0.2286(2)	0.1120(8)	1.8(2)	5.7(4)	3.0(3)	0.4(3)	–0.8(2)	–0.8(3)
N(2)	1.7723(11)	0.0761(2)	1.3856(8)	1.7(2)	2.2(3)	2.9(3)	–0.1(2)	–0.6(2)	–0.3(2)
C(1)	–0.0042(13)	0.2185(2)	0.2429(8)	1.7(3)	1.6(3)	2.2(3)	0.2(2)	–0.5(12)	0.6(2)
C(2)	0.1733(14)	0.2494(3)	0.3374(9)	1.2(3)	4.8(4)	1.9(3)	0.1(3)	–0.4(3)	0.3(3)
C(3)	0.1334(17)	0.2980(3)	0.3045(10)	3.4(4)	5.1(4)	2.2(4)	0.1(4)	–0.6(3)	0.1(3)
C(4)	–0.1288(20)	0.3165(4)	0.1805(12)	4.9(5)	7.8(7)	3.2(4)	0.0(5)	–1.3(4)	–0.4(5)
C(5)	–0.3121(16)	0.2793(3)	0.0841(11)	3.1(4)	5.7(5)	2.8(4)	1.0(4)	–0.7(3)	1.0(4)
C(6)	0.4543(11)	0.2351(2)	0.4985(8)	1.1(2)	1.9(3)	2.1(2)	–0.5(2)	–0.1(2)	–0.5(2)
C(7)	1.5181(15)	0.0962(3)	1.2355(9)	1.8(3)	5.1(5)	1.3(3)	–0.5(3)	–0.6(3)	–0.1(3)
C(8)	1.3242(15)	0.0566(3)	1.1367(9)	1.8(3)	4.0(4)	2.9(3)	–0.2(3)	–1.4(3)	–0.1(3)
C(9)	0.3842(16)	0.0066(3)	0.1794(10)	3.8(4)	4.9(4)	1.9(3)	1.1(4)	–0.7(3)	–0.3(3)
C(10)	1.6505(15)	–0.0044(2)	1.3374(10)	3.1(3)	2.0(4)	2.7(3)	0.0(3)	–0.8(3)	–0.2(3)
C(11)	1.8337(15)	0.0324(2)	1.4351(9)	3.1(3)	2.2(4)	2.1(3)	–0.0(3)	–0.5(3)	–0.9(3)
C(12)	1.0477(16)	0.0764(3)	0.9793(10)	2.8(4)	4.8(6)	2.2(3)	–0.6(4)	–1.0(3)	0.7(3)

TABLE III. Selected Interatomic Distances (Å) and Angles (°) with their Standard Deviations.

Environment of copper					
Cu(1)–O(1)	2.577(6)	O(2)–Cu(1)–O(5)	175.8(2)	O(1)–Cu(1)–O(2)	88.8(2)
Cu(1)–O(4)	2.468(6)	O(2)–Cu(1)–O(7)	89.5(2)	O(1)–Cu(1)–O(5)	88.3(2)
Cu(1)–O(2)	1.926(5)	O(2)–Cu(1)–O(8)	89.3(2)	O(1)–Cu(1)–O(7)	90.1(2)
Cu(1)–O(5)	1.957(4)	O(5)–Cu(1)–O(7)	93.5(2)	O(1)–Cu(1)–O(8)	85.7(2)
Cu(1)–O(7)	1.866(6)	O(5)–Cu(1)–O(8)	87.4(2)	O(4)–Cu(1)–O(2)	90.2(2)
Cu(1)–O(8)	2.000(6)	O(7)–Cu(1)–O(8)	175.6(3)	O(4)–Cu(1)–O(5)	92.8(2)
		O(1)–Cu(1)–O(4)	178.9(2)	O(4)–Cu(1)–O(7)	89.6(2)
				O(4)–Cu(1)–O(8)	94.6(2)
Pyridine N-oxido groups					
N(1)–O(1)	1.345(8)	O(1)–N(1)–C(1)	125.5(6)		
N(1)–C(5)	1.428(11)	O(1)–N(1)–C(5)	120.3(5)		
N(1)–C(1)	1.310(7)	C(1)–N(1)–C(5)	114.1(6)		
C(1)–C(2)	1.251(9)				
C(2)–C(3)	1.379(11)				
C(3)–C(4)	1.402(11)				
C(4)–C(5)	1.394(12)				
N(2)–O(4)	1.321(7)	O(4)–N(2)–C(7)	108.8(5)		
N(2)–C(11)	1.265(9)	O(4)–N(2)–C(11)	121.9(5)		
N(2)–C(7)	1.469(8)	O(7)–N(2)–C(11)	129.2(6)		
C(7)–C(8)	1.473(10)				
C(8)–C(9)	1.422(10)				
C(9)–C(19)	1.459(9)				
C(10)–C(11)	1.386(9)				
Carboxylato groups					
C(6)–C(2)	1.539(8)	O(2)–C(6)–O(3)	122.5(5)		
C(6)–O(2)	1.265(8)	O(2)–C(6)–C(2)	114.9(5)		
C(6)–O(3)	1.292(8)	O(3)–C(6)–C(2)	122.6(6)		
C(12)–C(8)	1.559(9)	O(5)–C(12)–O(6)	135.2(7)		
C(12)–O(5)	1.191(10)	O(5)–C(12)–C(8)	115.4(6)		
C(12)–O(6)	1.229(9)	O(6)–C(12)–C(8)	109.1(7)		

ments to follow the decomposition of the crystal. Even though the crystal was encased in glue it decomposed slowly with the release of water.

At the end of the data collection the intensity of the standard reflection had decreased by 43 per cent. The data were corrected for Lorentz and polarisation factors but not for absorption effects.

Structure determination

The structure was solved by MULTAN direct methods [14]. MULTAN gave all non-hydrogen atoms except some of the lattice water oxygens. The refinement of the structure carried out by the X-Ray System programs [15] and a Univac 1100/10 computer led to a final *R*-value of 0.087. The scattering factors for Cu, C, N, O were those of Cromer and Mann [16] and for hydrogen atoms those reported by Stewart *et al.* [17]. No attempt was made to locate the hydrogen atoms.

The final atomic coordinates and anisotropic thermal parameters with their standard deviations are given in Table II. Lists of structure factors are available from the author.

Description of the Structure and Discussion

The title complex crystallizes as light green lamellar plates and decomposes in air with loss of water. It has a polynuclear chain structure. The labeling and the structure of the $[Cu(N\text{-}nicO)_2(H_2O)_2]\cdot 4H_2O$ unit are shown in Fig. 1 and bond lengths and angles are listed in Table III. The copper atoms have a distorted octahedral coordination geometry, the coordination polyhedron being elongated axially.

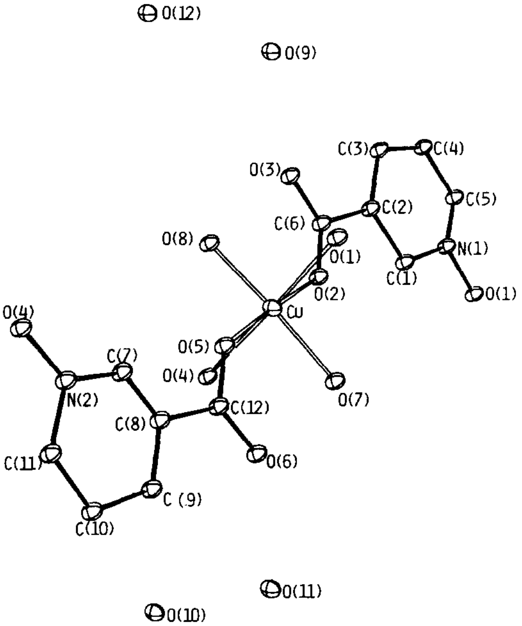

Fig. 1. The atomic labelling scheme of $[Cu(N\text{-}nicO)_2(H_2O)_2] \cdot 4H_2O$.

TABLE IV. The Hydrogen Bonds.

Hydrogen Bond	O–O Distance, Å
O(9)···O(10)^e	2.890(10)
O(9)···O(12)^a	2.767(8)
O(10)···O(6)^d	2.704(8)
O(10)···O(11)^c	2.693(11)
O(11)···O(10)^b	2.869(10)
O(12)···O(3)^d	2.807(9)
O(12)···O(9)^b	2.826(10)
O(12)···O(11)^d	2.807(9)

symmetry operations:

^{a}1 + x, y, z
^{b}x, y, z
^{c}−1 + x, y, z
^{d}−x + 1, y + ½, −z + 1
^{e}−x + 1, y + ½, −z

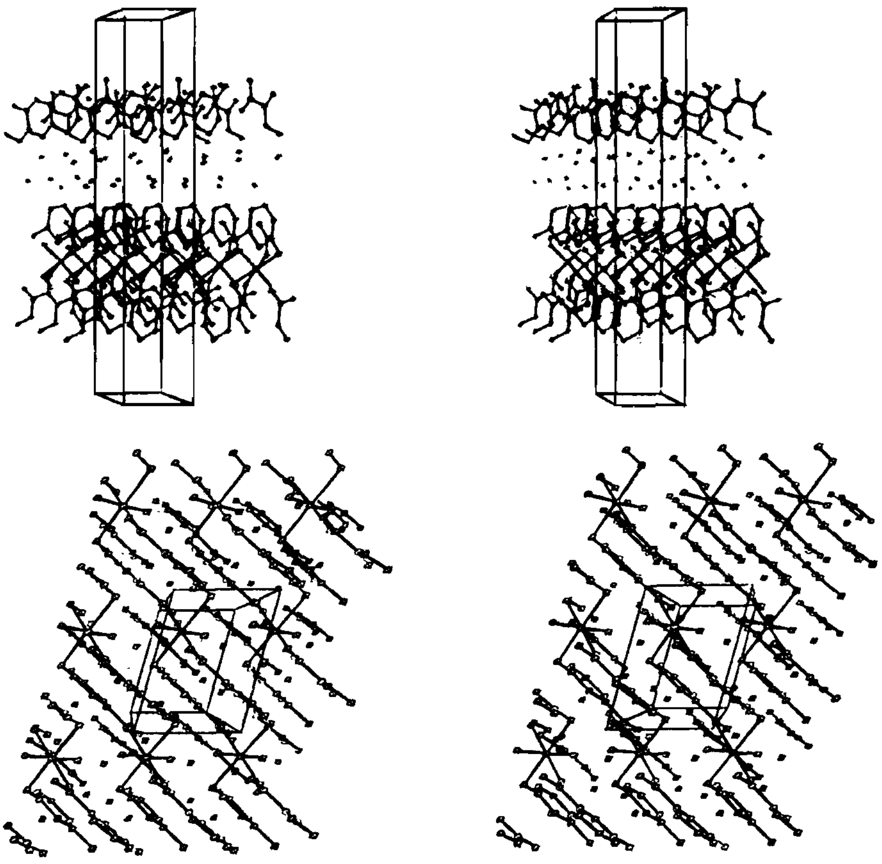

Fig. 2. A stereoview of the packing of the $\{[Cu(N\text{-}nicO)_2(H_2O)_2] \cdot 4H_2O\}$ chains in the unit cell a) in the *ab* plane, b) in the *ac* plane.

TABLE V. TG Data for $[Cu(N\text{-}nicO)_2(H_2O)_2]\cdot 4H_2O$.

Loss	In Fig.	Temperature °C	Weight loss	
			Calculated, %	Measured, %
$2H_2O$	I	25–39	8.66	5.5
$2H_2O$	II	39–83	8.66	8.9
$2H_2O$	III	115–144	8.66	9.6
$4H_2O$	I + II		17.32	14.4
$6H_2O$	I + II + III		25.99	23.8

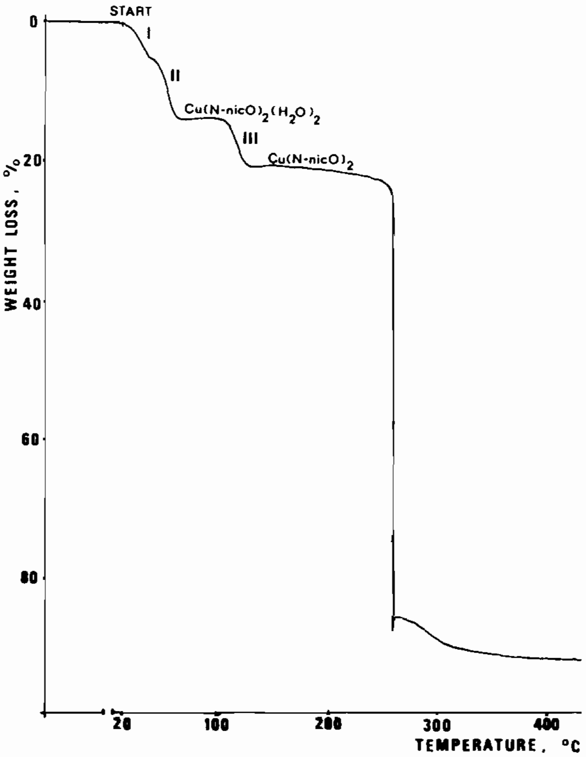

Fig. 3. The TG curve of $[Cu(N\text{-}nicO)_2(H_2O)_2]\cdot 4H_2O$. Sample weight 9.58 mg; atmosphere: static air; heating rate 2.5°/min.

Two nicotinato N-oxido groups are coordinated equatorially through one carboxylato oxygen to the copper ion, with bond lengths 1.926 and 1.957 Å; and two are coordinated axially through the N-oxide oxygen atom, with bond lengths 2.468 and 2.577 Å. The axial Cu–O bond lengths are appreciably longer than the equatorial ones, indicating a weak interaction. In diaquadi-μ-hydroxobis-μ-(nicotinato N-oxide)bis-μ(nicotinato N-oxido)tricopper(II) the bond between copper and the N-oxido oxygen is also very long, 2.426 Å. Nicotinato N-oxido ligands form a double bridge between adjacent copper ions, such that N-nicO is joined through one carboxylato oxygen equatorially to one copper ion and through the N-oxido oxygen axially to the other copper ion. Zig-zag chains are formed and arranged in tightly packed layers, between which there is a layer of lattice water molecules. The packing in the unit cell is shown in Fig. 2a and b. Of the six water molecules in one structural unit, two are coordinated to the copper ion and four are lattice waters. Two of the lattice water molecules are joined by hydrogen bonds to the carboxylato oxygen atoms not bonded to copper, and the other two are joined by hydrogen bonds to the first two. The hydrogen bonds are presented in Table IV. The clear lattice water layer explains the lamellar structure of the crystal as well as the easy decomposition. Thermal decomposition studies showed that the four lattice waters leave first from the complex (Fig. 3 and Table V). The first plateau appears in the TG curve at 83–115 °C, corresponding to $Cu(N\text{-}nicO)_2\cdot(H_2O)_2$. The next decomposition takes place above 115 °C, resulting in dehydrated $Cu(N\text{-}nicO)_2$. This decomposes at 250 °C, with the rapid loss of all organic material.

IR spectra of the complex and two decomposition intermediates are shown in Fig. 4 and the important absorptions are listed in Table VI. The IR spectrum of the first intermediate, $Cu(N\text{-}nicO)_2(H_2O)_2$, shows only slight changes compared with the IR spectrum of the original undecomposed complex. In both spectra ν(OH) absorptions are very strong and broad. In $[Cu(N\text{-}nicO)_2(H_2O)_2]\cdot 4H_2O$ the ν(OH) band is at about 3400 cm^{-1}, and in $Cu(N\text{-}nicO)_2(H_2O)_2$ it is in the region 3000–3100 cm^{-1}. The loss of the lattice water causes a visible difference in the region 500–800 cm^{-1}, where absorptions of N-nicO become sharper. In the dehydrated intermediate, $Cu(N\text{-}nicO)_2$, the important absorptions ν_{asym}(COO) and ν_{sym}(COO) can be seen to have shifted.

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TABLE VI. Some Infrared Absorption Bands (cm^{-1}) for [Cu(N-nicO)$_2$·2H$_2$O]·4H$_2$O and its TG Intermediates.

Compound	ν_{asym}(COO)	ν_{sym}(COO)	ν(OH)	δ(H–O–H)	H–O–H wagging, rocking, stretching	ν(NO)	δ(NO)
[Cu(N-nicO)$_2$·2H$_2$O]·4H$_2$O	1630	1393	3400	1603	700–750	1233	797
[Cu(N-nicO)$_2$·2H$_2$O]	1630	1393	3000–3100	1600	560–600	1233	797
[Cu(N-nicO)$_2$]	1665	1375				1223	800

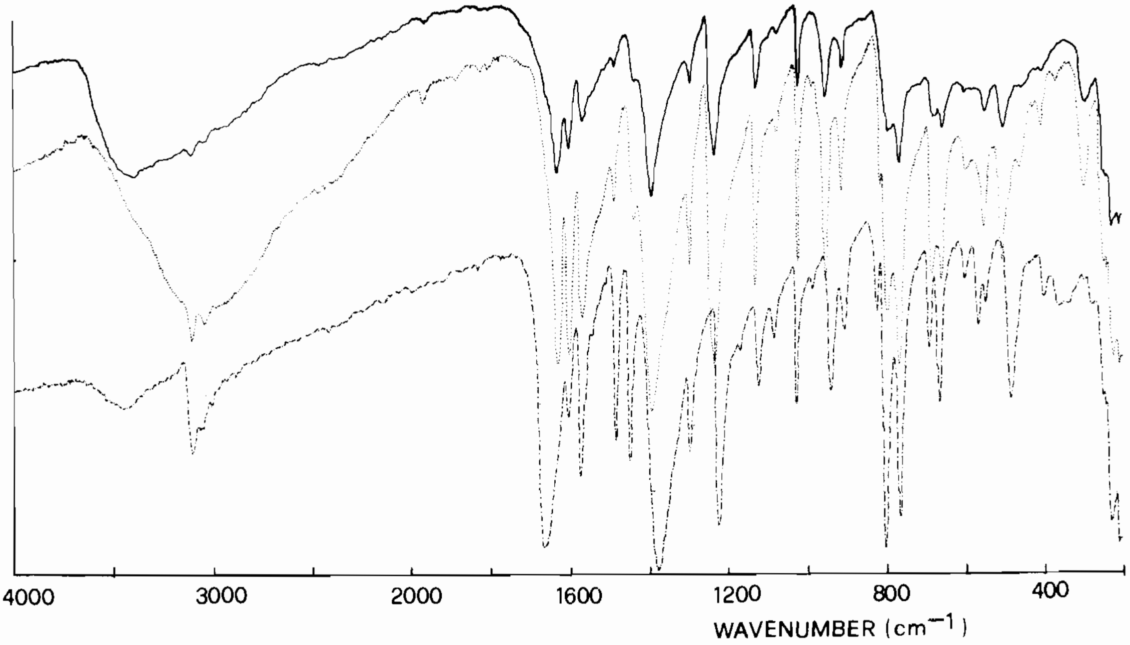

Fig. 4. The infrared spectra of [Cu(N-nicO)$_2$(H$_2$O)$_2$]·4H$_2$O (———) and its TG intermediates, Cu(N-nicO)$_2$(H$_2$O)$_2$ (······) and Cu(N-nicO)$_2$ (–·–·–).

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