The Crystal and Molecular Structures of

Tetraaquabis(nicotinato *N*-oxide)cobalt(II) and -nickel(II)

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The crystal and molecular structures of tetra-aquabis(nicotinato *N*-oxide)cobalt(II) and -nickel(II), [M(*N*-nicO)$_2$(H$_2$O)$_4$], M=Co, Ni, have been determined by X-ray techniques. The least squares refinement led to a final *R*-value of 0.049 for the cobalt complex.

Tetraaquabis(nicotinato *N*-oxide)cobalt(II) and -nickel(II) are isomorphous compounds. The crystals are monoclinic. The space group is *P*2$_1$/*c*, with *Z*=2 and cell dimensions are *a*=8.896(5), *b*=13.363(9), *c*=6.719(3) Å, *β*=109.40(4)° for the cobalt complex and *a*=8.852(9), *b*=13.277(16), *c*=6.657(5) Å and *β*=108.79(7)° for the nickel complex. Two nicotinato *N*-oxide ligands are coordinated to the central metal atom through one carboxylato oxygen atom, and there are four aqua ligands. The coordination geometry is slightly distorted octahedral.

Several metal complexes with nicotinic acid *N*-oxide (*N*-nicOH) have been synthesized and characterized.[1-11] In particular the kinetic, magnetic and spectral properties of these complexes have been studied. Chloride and perchlorate adducts have been prepared in organic (non-aqueous) media, including ethanol, ethanol−triethylorthoformate and *N,N*-dimethylformamide.[2,3,6-8] Sodium and magnesium compounds have been studied for their therapeutic properties.[9]

Divalent 3*d* metal complexes with nicotinic acid *N*-oxide have been described as hexacoordinated, linear, polynuclear complexes of the type [M(N-nicO)$_2$(H$_2$O)$_2$]$_n$ · *m*H$_2$O (*m*=2*n* for M=Mn, Fe, Co, Ni, Cu, and *m*=3*n* for M=Zn).[4] The authors assume that the nicotinate *N*-oxide groups act as bridging ligands coordinating

through N−O oxygen atoms and one COO oxygen atom. Earlier, in a study on the cobalt complex, it was suggested that the nicotinato *N*-oxide ligand is coordinated only through one carboxylic oxygen atom.[1]

Polymeric Cu(II) complexes were the first metal complexes with nicotinic acid *N*-oxide to be subjected to X-ray structure analysis.[10,11,23] In these complexes nicotinate *N*-oxide acts as a bidentate bridging ligand coordinating either through both carboxylato oxygen atoms or through one carboxylato oxygen and the N−O oxygen atom to different copper atoms. Polymerization occurs *via* *N*-oxide groups and the Cu−O bond lengths are quite long (2.426−2.672 Å), indicating a rather weak interaction.

The present structure determination is of the isomorphous Co(II) and Ni(II) complexes with nicotinic acid *N*-oxide and proves the hypothesis of Euler *et al.*[1] about the mode of coordination of the nicotinate *N*-oxide group to the cobalt atom. The structures of isomorphous Co(II) and Ni(II) compounds of picolinic and isonicotinic acid *N*-oxides have been reported earlier.[12-14]

EXPERIMENTAL

Preparation of the complexes. [Co(*N*-nicO)$_2$(H$_2$O)$_4$] and [Ni(*N*-nicO)$_2$(H$_2$O)$_4$] crystals were prepared by the procedure used to synthesize metal complexes of pyridine monocarboxylic acid *N*-oxides.[4,15] A slightly modified crystallization was made from dilute solutions. The crystals of the Ni(II) complex were not, however, of satisfactory quality for single crystal X-ray analy-

Table 1. Crystal and refinement data of [Co(N-nicO)$_2$(H$_2$O)$_4$] and [Ni(N-nicO)$_2$(H$_2$O)$_4$].

	[Co(C$_6$H$_4$NO$_3$)$_2$(H$_2$O)$_4$]	[Ni(C$_6$H$_4$NO$_3$)$_2$(H$_2$O)$_4$]
F.W.	407.20	406.97
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.896(5)	8.852(9)
b	13.363(9)	13.277(16)
c	6.719(3)	6.657(5)
β (°)	109.40(4)	108.79(7)
Z	2	2
V (Å^3)	753.4	740.7
μMo$K\alpha$(cm^{-1})	12.51	
Collection mode	$\theta/2\theta$	
Radiation	Mo$K\alpha$	
Scan range	4°<2θ<60°	
Scan rate (°min^{-1})	1.0→15.0	
Refl. meas.	2743	
obs. (I>3σ(I)	1591	
F(000)	418	
$R(=\Sigma\| |F_o|-|F_c| \|/\Sigma|F_o|)$	0.049	

Table 2. Final positional parameters for [Co(N-nicO)$_2$(H$_2$O)$_4$] including hydrogen atoms and U_{eq} ($\times 10^3$) (Å^2) and U_{iso}($\times 10^2$) for hydrogen atoms.

Atom	x	y	z	U_{eq}[a]
Co	1.0000	0.0000	1.0000	1.80(1)
O(1)	0.6613(2)	0.9609(1)	0.3359(2)	2.81(7)
O(2)	0.8240(2)	0.1116(1)	−0.0610(2)	2.58(6)
O(3)	0.9752(2)	0.2386(1)	0.1113(2)	2.87(7)
O(4)	0.8810(2)	0.5727(1)	0.2195(2)	3.47(8)
O(5)	0.1173(2)	0.0919(1)	0.8418(3)	3.65(8)
C(1)	0.7449(2)	0.1254(1)	0.4031(3)	2.22(8)
C(2)	0.2869(2)	0.7269(1)	0.1127(3)	2.09(8)
C(3)	0.4412(2)	0.7587(1)	0.2128(3)	2.59(9)
C(4)	0.4401(2)	0.1887(1)	0.2071(3)	2.81(9)
C(5)	0.4767(2)	0.0881(1)	0.2260(3)	7.76(9)
C(6)	0.8492(2)	0.2975(1)	0.4877(3)	2.17(8)
N(1)	0.3730(2)	0.5593(1)	0.1803(3)	2.32(7)
				U_{iso}
H(1)	0.145(3)	0.599(2)	0.037(3)	2.9(6)
H(2)	0.524(3)	0.333(2)	0.273(4)	3.0(6)
H(3)	0.664(2)	0.715(1)	0.369(3)	1.4(5)
H(4)	0.409(3)	0.045(2)	0.185(4)	4.6(8)
H(5)	0.802(4)	0.933(2)	0.190(5)	6.9(10)
H(6)	0.060(3)	0.367(2)	0.264(4)	4.7(8)
H(7)	0.810(4)	0.566(2)	0.109(5)	6.8(9)
H(8)	0.081(4)	0.122(2)	0.275(5)	7.8(10)

[a] $U_{eq}=\frac{1}{3}\sum_i U_{ii}$

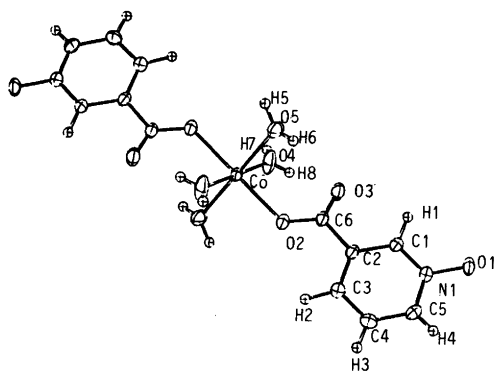*Fig. 1.* The labelling and structure of [Co(*N*-nicO)$_2$(H$_2$O)$_4$]. Thermal ellipsoids are drawn to enclose the 50 % probability level.

sis which was, therefore, performed for the Co(II) complex only.

Data collection. The crystal and refinement data are given in Table 1. The crystal and intensity data were measured on a Syntex *P*2$_1$ four-circle diffractometer using graphite monochromatized MoKα radiation. The unit cell parameters were calculated by least squares refinement of 15 high order reflections.

The data were corrected for Lorentz and polarization factors. Absorption correction was not made.

Structure determination. The structure of the Co(II) complex was solved by direct methods[16] and Fourier techniques and refined by block diagonal matrix least squares methods with anisotropic temperature factors for all nonhydrogen atoms. All hydrogen atoms were located by difference Fourier syntheses. The final *R*-value was 0.049.

All calculations were carried out with X-Ray System programs[17] on a UNIVAC 1100/60 com-

puter. The scattering factors for Co, C, N and O were those of Cromer and Mann[18] and for hydrogen atoms those reported by Stewart *et al.*[19]

Table 2 presents the final atomic coordinates and the thermal parameters (U_{eq} and U_{iso}) with their standard deviations for the cobalt compound. Lists of structure factors and anisotropic thermal parameters are available from the author upon request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

The title compounds tetraaquabis(nicotinato *N*-oxide)cobalt(II) and -nickel(II) are isomorphous complexes based on the crystal data, just as are the cobalt and nickel compounds of picolinic and isonicotinic acid *N*-oxides: diaquabis(picolinato *N*-oxide)cobalt(II) and -nickel(II)[12] and hexaaquacobalt(II) and hexaaquanickel(II) isonicotinate *N*-oxide.[13]

Joined monodentately to the central metal atom are two nicotinato *N*-oxide ligands, through one carboxylato oxygen atom, and four aqua ligands. This is the same kind of coordination mode as the isonicotinato N-oxide ligand has in [Mn(*N*-inico)$_2$(H$_2$O)$_4$].[14] The coordination geometry is slightly flattened octahedral. The labelling and structure of the molecule are given for [Co(*N*-nicO)$_2$(H$_2$O)$_4$] in Fig. 1 and a stereoview of the packing in the unit cell is shown in Fig. 2. Bond distances and angles are presented in Table 3.

The aqua ligands form intramolecular hydrogen bonds with uncoordinated carboxylato oxygen atoms, and hydrogen bonds between the aqua ligands and the *N*-oxide oxygen atoms join complex molecules to each other. The hydrogen bonds are listed in Table 4.
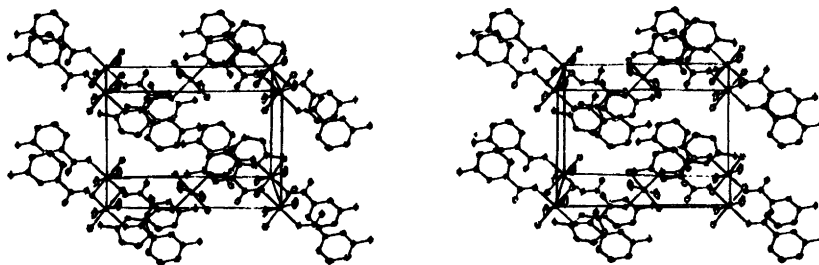

Fig. 2. Stereoview of the packing of [Co(*N*-nicO)$_2$(H$_2$O)$_4$] within the unit cell. Hydrogen atoms have been excluded for clarity.

Table 3. Selected bond distances (Å) and bond angles (°) with their standard deviations for [Co(N-nicO)$_2$(H$_2$O)$_4$].

Environment of central metal			
Co−O(2)	2.102(1)	O(2)−M−O(4)	88.09(6)
Co−O(4)	2.072(1)	O(2)−M−O(5)	87.06(6)
Co−O(5)	2.113(2)	O(5)−M−O(4)	90.25(6)
		O(4)−M−O(2)	91.91(6)
		O(4)−M−O(5)	89.75(6)
		O(5)−M−O(2)	92.94(6)
Pyridine *N*-oxide group			
N(1)−O(1)	1.347(2)	O(1)−N(1)−C(1)	119.0(1)
N(1)−C(1)	1.344(2)	O(1)−N(1)−C(5)	119.1(1)
N(1)−C(5)	1.331(2)	C(1)−N(1)−C(5)	121.9(2)
C(1)−C(2)	1.384(2)	N(1)−C(1)−C(2)	120.2(1)
C(2)−C(3)	1.379(3)	C(1)−C(2)−C(3)	119.0(2)
C(3)−C(4)	1.379(3)	C(2)−C(3)−C(4)	119.4(2)
C(4)−C(5)	1.381(3)	C(3)−C(4)−C(5)	119.9(2)
Carboxylato group			
C(6)−C(2)	1.508(2)	O(2)−C(6)−O(3)	126.1(2)
C(6)−O(2)	1.260(2)	O(2)−C(6)−C(2)	116.1(1)
C(6)−O(3)	1.249(2)	O(3)−C(6)−C(2)	117.8(1)

Table 4. Hydrogen bonds

Atoms	Distances (Å)			Angle (°)
A−H⋯B	A−H	H⋯B	A⋯B	AHB
O(4)−H(7)⋯O(1)	0.80(3)	1.91(3)	2.705(2)	172(3)
O(4)−H(8)⋯O(3)	0.73(3)	1.96(3)	2.624(2)	150(3)
O(5)−H(5)⋯O(1)	0.88(3)	1.87(4)	2.713(3)	161(3)
O(5)−H(6)⋯O(3)	0.81(2)	2.01(2)	2.799(2)	163(2)

The coordination of picolinato, nicotinato and isonicotinato *N*-oxide ligands in Co(II) and Ni(II) compounds is presented schematically in Fig. 3. Co−O bond distances are in agreement with the corresponding cobalt(II) bond distances in [Co(*N*-picO)$_2$(H$_2$O)$_2$] (2.061(1)−2.148(1)Å) and [Co(H$_2$O)$_6$] (*N*-inicO)$_2$ (2.052(2)−2.092(2) Å). Both the N−O and C−O bond distances are shortest for [Co(H$_2$O)$_6$] (*N*-inicO)$_2$. The C−C(ring) distances are similar in three compounds.

The positions of the substituents of pyridine monocarboxylic acid *N*-oxides in the ring appear to play a significant role in the coordination chemistry of the Co(II) and Ni(II) compounds.

The substituents, the *N*-oxide and carboxylic groups are in the *ortho*-position in picolinic acid *N*-oxide and a stable 6-membered ring is generated through the *N*-oxide group and one carboxylato oxygen atom when the complex forms.[13] In nicotinic acid *N*-oxide the *N*-oxide group is in *meta*-position to the carboxylic group and does not coordinate to the cobalt and nickel atoms. Coordination occurs only through one carboxylato oxygen atom. In isonicotinic acid *N*-oxide, where the *N*-oxide and carboxylic groups are in *para*-position, neither group is coordinated to the Co(II) or Ni(II) ion,[12] nor to Fe(II),[14] Mg(II) or Zn(II)[20] ion; rather the compounds formed are ionic with hexaaquametal(II) cations and isonico-
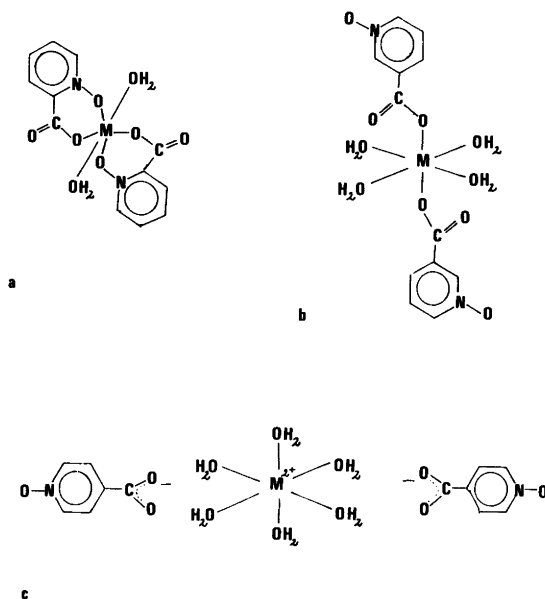
Fig. 3. Cobalt(II) and nickel(II) compounds of pyridine monocarboxylic acid *N*-oxides schematically.
(a) [M(*N*-picO)₂ (H₂O)₂], M=Co(II), Ni(II);[12] (b) [M(*N*-nicO)₂ (H₂O)₄], M=Co(II), Ni(II);
(c) [M(H₂O)₆] (*N*-inicO)₂, M=Co(II), Ni(II).[13]

tinate *N*-oxide anions. The coordination ability of the *N*-oxide group of pyridine monocarboxylic acid *N*-oxides clearly decreases in the order picolinic acid *N*-oxide > nicotinic and *N*-oxide > isonicotinic acid *N*-oxide in compounds formed in aqueous solutions.[10–14,20–22]

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