

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ  
RESEARCH REPORT No. 12

**X-RAY STRUCTURAL STUDIES ON SOME  
DIVALENT 3d METAL COMPOUNDS OF PICOLINIC  
AND ISONICOTINIC ACID N-OXIDES**

**BY  
PEKKA KNUUTTILA**

Academic Dissertation  
for the Degree of  
Doctor of Philosophy



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## PREFACE

The present work was carried out in the Department of Chemistry, University of Jyväskylä, during the years 1979 - 1981.

I wish to express my sincere thanks to Dr. Jussi Valkonen for his valuable assistance and advice in constructing the computer program system for structure determinations, and to Mr. Kauko Saarinen, M.Sc., for his help in adapting the plotter program.

My thanks also to Mrs. Anne Räsänen, M.A., M.Ed. and Dr. Kathleen Ahonen for correcting the language.

My wife, Hilikka Knuuttila, Ph.Lic., has provided me with astute criticism and unfailing support during this work and to her I express my deep gratitude.

Jyväskylä, December 1981

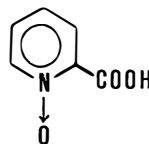
ERRATA

page	line	is:	should be:
CONTENTS	30-31	$M(N\text{-inicO})_2$	$M(N\text{-picO})_2(H_2O)_2$
8	1	(N-nicotinato)	(nicotinato-N)
8	4	(N-isonicotinato)	(isonicotinato-N)
8	5	(picolinate)	(picolinato)
11	8	formof	form of
31	3	icluding	including
33	4	Cc	Cc
33	13	call	cell
33	23	trans	trans
36	Fig.5.		central metal Mn
37	5	04-Mn-05	04-Mn-05'
37	6	04-Mn-05'	04-Mn-05
44	7	distances are 1.97 and	distance is 1.97,
46	10	1.92(4)	1.98(4)
46	11	1.95(1)	1.94(1)

Abbreviations

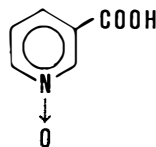
N-picOH = picolinic acid N-oxide,

N-picO (anion) pyridine 2-carboxylic  
acid 1-oxide



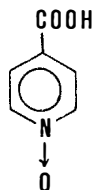
N-nicOH = nicotinic acid N-oxide,

N-nicO (anion) pyridine 3-carboxylic  
acid 1-oxide



N-inicOH = isonicotinic acid N-oxide,

N-inicO (anion) pyridine 4-carboxylic acid  
1-oxide



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## ABSTRACT

Nine structures of 3d metal complexes of picolinic and isonicotinic acid N-oxides have been solved for this study.

Bis(picolinato N-oxide)diaquamanganese(II), cobalt(II) and nickel(II) form an isomorphic series, from which the corresponding copper(II) complex differs, probably due to Jahn-Teller distortion. In all four complexes the picolinic acid N-oxide coordinates to the metal ion through the N-O oxygen and one of the (COO) oxygens, forming a stable six-membered chelate ring.

Isonicotinic acid N-oxide can join to the metal ions in many different ways. In trans-bis(isonicotinato N-oxide) tetraaquamanganese(II) the ligand coordinates to the central metal ion only through one of the carboxylic oxygens.

Bis(isonicotinate N-oxide)hexaaquairon(II), -cobalt(II)<sup>1</sup> and -nickel(II)<sup>1</sup> belong to an isomorphic series where the metal ion forms an hexaaqua cation with coordinated water molecules. There is no direct coordination between metal ions and isonicotinate N-oxide and the isonicotinate N-oxide anion is present in these structures instead.

In di- $\mu_3$ -hydroxo- $\mu$ -sulfato-tetrakis- $\mu$ -(isonicotinato N-oxide)tetraquatetracopper(II)<sup>2</sup> the isonicotinato N-

oxide ligand forms bridges between copper atoms coordinating through both carboxylic oxygens. This entirely new copper(II) complex exhibits interesting features, such as the rare mode of coordination of the sulfato group and the threefold bridge of the hydroxo group.

## INTRODUCTION

### 1. General

In 1912 von Laue discovered the phenomenon of X-ray diffraction by crystals, proving thereby the wave nature of X-rays and providing a new method for investigating the structure of solid matter.

W. L. Bragg immediately attacked the problem of crystal structure with this new tool of X-ray diffraction and, in the following year, solved the structures of NaCl, KCl, KBr and KI. These were the first complete crystal structure determinations ever made. During the first half-century following its invention, however, the method could seldom be applied, and even then under restricted conditions. The execution of one structure determination took several months, in some cases even a few years. Moreover, the results were of limited accuracy and not always unambiguous.

The situation has dramatically changed during the last 10 to 15 years, with the development of diffraction equipments and computer programs specially designed for structure determinations. One of the most advanced programs is the MULTAN program package.

The modern method of X-ray structure analysis can now be said to provide the most accurate and detailed

information on molecular and crystal geometries.

During recent years the number of publications on crystal and molecular structures solved by the X-ray diffraction technique has increased enormously. The X-ray technique is a powerful tool in chemistry, physics, biology, medicine, geology, metallurgy, fibre technology, and several other areas as well.

The aim of this work has been to study the structures of some 3d transition metal compounds of picolinic acid N-oxide and isonicotinic acid N-oxide by using the X-ray technique. Accurate structure determinations have not appeared in the literature except for those undertaken in this chemistry department.<sup>1,2,3</sup>

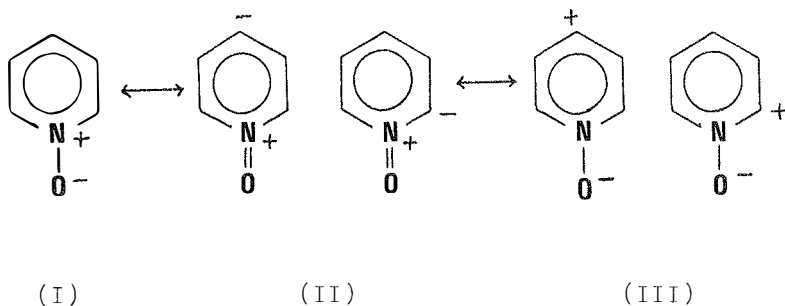
Pyridine carboxylic acid N-oxides are of great interest from coordination point of view since they include two different coordinating groups, the carboxylate group and the N-oxide group.

## 2. The coordination properties of pyridine N-oxides

N-oxidation of the pyridine nitrogen leads to significant alternation of the reactivity in the aromatic ring, owing to a reversal in the electron density distribution about the ring. The  $N^+-O^-$  group is strongly polarizable in both directions and can act either as an electron attracting group or as an electron donating

group, thereby facilitating both electrophilic and nucleophilic substitutions.<sup>4</sup>

In unsubstituted pyridine N-oxides the lone electron pair of the nitrogen is on the  $sp^2$  hybridized orbital, before formation of the N-O bond, with the result that the N-O bond is in the same plane as the aromatic ring, and the oxygen  $2p\pi$  electrons interact directly with the  $\pi$ -electron system of the ring. This situation can be represented by canonical structures (I), (II) and (III).



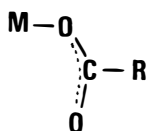
An electron withdrawing substituent on the heterocycle causes the canonical form (II) to become dominant, whereas an electron donating substituent tends to increase the proportion of the canonical form (III).<sup>5-7</sup> The double-bond character of the N-O bond is increased by the influence of the electron withdrawing substituent. For instance, the N-O bond length in 4-nitropyridine N-oxide

is  $1.26 \text{ \AA}^8$ , and the same bond length being in the unsubstituted pyridine N-oxide is  $1.37 \text{ \AA}^9$

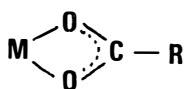
### 3. The nature of carboxylic coordination

The carboxyl group can coordinate to a metal ion in a number of ways: as a unidentate ligand (IV below)<sup>3,10</sup>, as a chelating ligand (V),<sup>11-13</sup> as a bridging bidentate ligand in a syn - syn (VI<sub>a</sub>)<sup>3</sup>, syn - anti (VI<sub>b</sub>)<sup>14</sup> or anti - anti (VI<sub>c</sub>)<sup>15</sup> configuration, as a monoatomic bridging ligand alone (VII),<sup>16</sup> as a bridging bidentate ligand with additional bridging (VIII),<sup>17</sup> and in many other ways as both a chelating and a bridging ligand (IX<sub>a</sub>, IX<sub>b</sub>).<sup>12,13,18</sup>

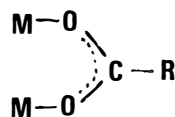
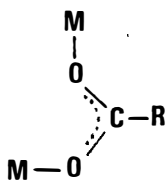
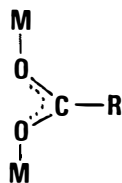
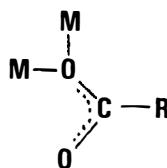
Ionic metal carboxylates are also well known.<sup>19,20</sup>



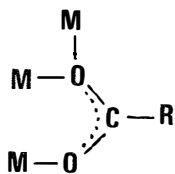
(IV)



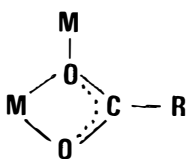
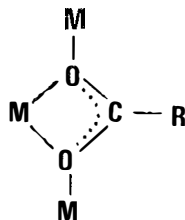
(V)

(VI<sub>a</sub>)(VI<sub>b</sub>)(VI<sub>c</sub>)

(VII)

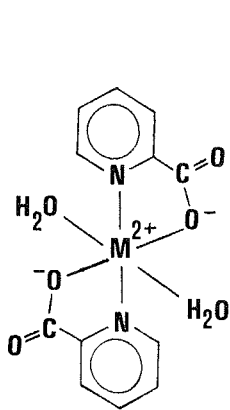


(VIII)

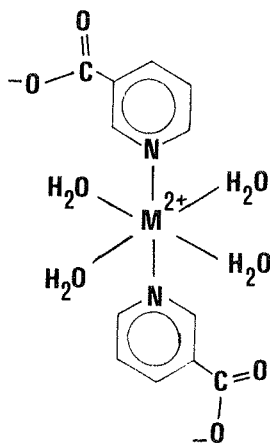
(IX<sub>a</sub>)(IX<sub>b</sub>)

#### 4. Structures of the metal complexes of pyridine carboxylic acids and pyridine N-oxides

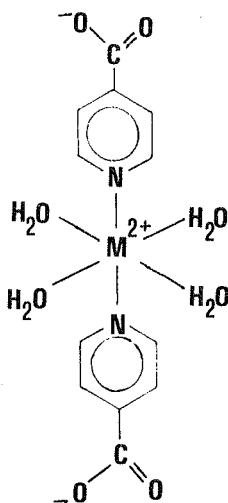
The structures of great number of complexes between pyridine monocarboxylic acids and metals of the first transition series have been solved by the X-ray diffraction technique. When a divalent metal ion serves as the central atom the following main structures are found:



(X)



(XI)



(XII)

In bis(N-nicotinato)tetraaquazinc(II)<sup>21</sup> and the corresponding cobalt(II) complex,<sup>22</sup> coordination takes place through the nitrogen atom, as in (XI). The structures of bis(N-isonicotinato)tetraaquazinc(II) and -cadmium(II)<sup>23</sup> correspond to (XII). In bis(picolate) diaquazinc(II)dihydrate and -nickel(II) complexes coordination occurs through the pyridine nitrogen atom and one of the (COO) oxygen atoms as in (X).<sup>24-26</sup>

In all these compounds the pyridine nitrogen atom behaves as a stronger coordinating group than the carboxylate group in 3- and 4-positions. When the carboxylate group is in 2-position a stable five membered ring is formed, and the carboxylate group then coordinates additionally through one of the (COO) oxygen atoms. Furthermore, (isonicotinato-N)-(isonicotinato-O) tetraaquamagnesium(II) is a compound known to have one ligand coordinating through its pyridine nitrogen atom and the other through one of the carboxylic oxygens.<sup>10</sup>

The structures of many transition metal complexes of pyridine N-oxides have been solved by the X-ray diffraction technique. In particular, the hexakis-(pyridine N-oxide)copper(II) and -zinc(II) complexes have been intensively studied with different anions. The  $\text{Cu}(\text{C}_5\text{H}_5\text{NO})_6^{2+}$  cation has been used to study the static and dynamic Jahn-Teller effect.<sup>27-29</sup> In the first transition series the metals from manganese to zinc



form  $M(C_5H_5NO)_6^{2+}$  ions and an isomorphic series when the anion is  $BF_4^-$  or  $ClO_4^-$ . The complexes all belong to the same space group  $R\bar{3}$ , and coordination occurs through the N-O oxygen.<sup>30-32</sup> The structures of tetrakis(pyridine N-oxide)copper(II) tetrafluoroborate and perchlorate have also been solved by X-ray technique.<sup>33</sup>

The oxygen atom of the pyridine N-oxide can act as a bridge between metal ions, as observed in tetrachlorobis[ $\mu$ -(pyridine N-oxide)]dicopper(II)<sup>34</sup> and in tetranitratobis[ $\mu$ -(pyridine N-oxide)]bis(pyridine N-oxide)dicopper(II).<sup>35</sup> Similarly in many complexes solved by Watson et al.<sup>36-38</sup> the N-oxide oxygen atom acts as a bridge. Also mixed ligand structures with pyridine N-oxide as one of the ligands have been studied.<sup>39</sup> The coordination in these mixed complexes is cis octahedral, whereas in the corresponding pyridine complex it is trans octahedral.

Several structures of the metal complexes of substituted pyridine N-oxides have been solved, too. Where the nitro group is in 4-position and the central metal ion is copper(II)<sup>40</sup> or where methyl groups in 2-, and 2,6-positions are the substituents and cobalt(II), zinc(II) or copper(II) is the central metal ion,<sup>41-43</sup> the coordination occurs through the N-oxide oxygen atom without bridge formation. But with  $CuCl_2$ , 2-methylpyridine N-oxide forms a polymer in which bridges of the

di- $\mu$ -chloro and di- $\mu$ -(N-O) oxygen atoms bind the copper atoms together.<sup>44</sup>

Pyridine N-oxide thus coordinates either as a unidentate ligand from the N-oxygen to the central metal ion or as a bridging bidentate ligand.

Some authors have used the structures of metal complexes of pyridine carboxylic acids and pyridine N-oxide to predict the structures of pyridine carboxylic acid N-oxide metal complexes.

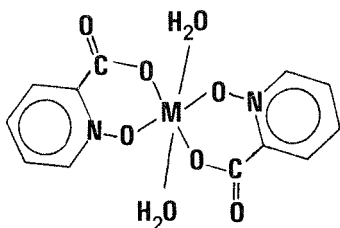
## 5. Coordination of the metal complexes of pyridine carboxylic acid N-oxides

Many metal complexes of pyridine carboxylic acid N-oxides have been synthesized, and their properties and structures studied by spectrometric and magnetic methods, for instance. However, there were no accurate structure determinations of these complexes to be found in the literature before those carried out in our laboratory by the X-ray diffraction methods.<sup>1-3</sup>

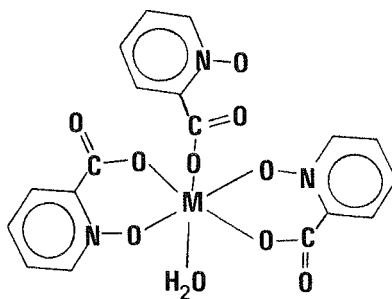
### 5.1. Complexes of picolinic acid N-oxide

In most cases, picolinic acid N-oxide acts as a bidentate ligand coordinating through the N-O oxygen atom and one of the (COO) oxygen atoms (XIII). The coordination is considered to occur in this way with

alkaline earth<sup>45</sup> and transition  $3d$  metal ions,<sup>45,46,49,50</sup> with lanthanoid,<sup>47</sup> and some actinoid ions<sup>48</sup> and with B(III).<sup>51</sup> In the complexes synthesized in glacial acetic acid additional coordination is believed to occur monodentately through one of the (COO) oxygens, when Cr(III) and Co(III) are the central metal ions (XIV).<sup>45</sup> However, for Mn(III) and Fe(III) a polymeric system based upon the anhydrous form of (XIV) may be possible.<sup>45</sup>



(XIII)



(XIV)

A chelating structure through both oxygen atoms of the carboxylic group has been considered in the anhydrous Mn(II) complex.<sup>49</sup>

Iaconianni et al.<sup>50</sup> published in 1979 their study on the  $3d$  metal perchlorates of the picolinic acid N-oxides. The complexes were synthesized in nonaqueous conditions ethanol-triethyl orthoformate (teof) serving as solvent. Hydrated metal perchlorates were used as metal source. According to their results Mn(II) and

Zn(II) form the complexes described in formula (XIII). Co(II), Ni(II) and Fe(III) complexes include one chelating N-picO and one N-picOH that coordinates only through the N-O oxygen, and further, three coordinated water molecules. The Cr(III) and Fe(II) complexes contain a total of three ligands per metal ion: two chelating and one unidentate N-picOH in Cr(III), and one chelating and two unidentate in Fe(II). Both include two coordinated water molecules. The unidentate ligands coordinate through N-O oxygen.

## 5.2. Complexes of nicotinic acid N-oxide

One of the first of the few studies on the metal complexes of nicotinic acid N-oxide describes the bis-(nicotinato N-oxide)tetraaquacobalt(II) complex which nicotinic acid N-oxide forms with  $\text{CoCl}_2$ .<sup>52</sup> In this complex nicotinate N-oxide coordinates unidentately to the cobalt atom through one carboxylic oxygen atom.<sup>53</sup>

Specca et al.<sup>54,55,57</sup> have studied the structures of nicotinic acid N-oxide complexes with divalent 3d metal ions. They claim that the nicotinic acid N-oxide anion coordinates through the N-O oxygen atom and one of the (COO) oxygen atoms to form polynuclear polymeric compounds. The Fe(II) and Fe(III) ions reportedly form their complexes with nicotinic acid N-oxide in the same way.<sup>58</sup> Gelfand et al.<sup>56</sup> have prepared the adduct of  $\text{CuCl}_2$  and nicotinic acid N-oxide in nonaqueous conditions. They

propose that a dinuclear dimer complex is formed in which eight nicotinic acid N-oxide molecules coordinate through the N-O oxygen atom. Two of the eight ligands act as bridges between adjacent copper atoms.

With lanthanoid compounds, nicotinic acid N-oxide is assumed to coordinate through all its oxygen atoms.<sup>59,60</sup>

The reaction of nicotinic acid N-oxide with  $UCl_4$  under highly acidic conditions leads to coordination through the N-O oxygen.<sup>61</sup>

In the structure of polymeric diaqua-di- $\mu$ -hydroxo-bis- $\mu$ -(nicotinato N-oxide)-bis- $\mu$ -(nicotinato N-oxido)-tricopper(II) solved by Hilikka Knuuttila<sup>3</sup> the nicotinate N-oxide acts as a bridging ligand and is coordinated bidentately through both carboxylate oxygen atoms, forming a bridge between copper atoms, and through one carboxylate oxygen atom and the N-oxide oxygen atom. The N-O oxygen - copper bond is very weak, being only 2.426(2) Å.

### 5.3. Complexes of isonicotinic acid N-oxide

The metal complexes of isonicotinic acid N-oxide were very little studied before the year 1979.

Uranium tetrachloride reacts with isonicotinic acid N-oxide coordinating through the N-O oxygen atom.<sup>61</sup> The reaction with Zeise's salt ( $Cl_3PtC_2H_4K$ ) in aqueous solution leads to a product in which coordination occurs

through the N-O oxygen atom.<sup>62</sup>

In 1979 Gelfand et al. published their wide article on transition metal complexes with isonicotinic acid N-oxide and their partial dehydration products.<sup>63</sup> Palepu<sup>64</sup> later confirmed their results. The complexes are characterized as polynuclear hexa- or pentahydrated, the central metal ion being hexacoordinated. An exception is the Cu(II) dihydrate complex in which coordination is assumed to be square planar. In all these complexes ligands are supposed to form single bridges between the adjacent metal ions, coordinating through the N-O oxygen atom and one of the carboxylate oxygen atoms.

Water molecules are either connected via hydrogen to the uncoordinated oxygen of the (COO) group or behave as aqua ligands. All the hexahydrates are supposed to have the same structure, but they cannot be characterized as isostructural compounds. In the lower hydrates the coordination type of the isonicotinic acid N-oxide is unaltered, but the water molecules are assumed to form bridges between the metal ions.

The structure of the anhydrous  $Mn(N-inicO)_2$  is supposed to be polynuclear in which some of the N-*inicO* ligands coordinate through all oxygens and the others bidentately through the N-O and one of the (COO) oxygens.<sup>55</sup> According to Gelfand et al.<sup>56</sup> the 1:1 adduct between

$\text{CuCl}_2$  and isonicotinic acid N-oxide formed in ethanol - teof mixture is apparently polymeric with the ligand functioning as a bridge and coordinating tridentately through all three of its oxygen atoms. The same authors have also studied the complexes of isonicotinic acid N-oxides and  $3d$  metal perchlorates prepared in ethanol - teof mixture.<sup>57</sup> These complexes are supposed to be polynuclear, with both unidentate terminal and bidentate bridging isonicotinic acid N-oxide ligands.

#### 6. Summary of the coordination in the metal complexes of pyridine carboxylic acid N-oxides

In complexes prepared in aqueous solutions picolinic acid N-oxide tends to form a stable six-membered ring (XIII p.11) and coordinates bidentately through the N-O oxygen and one of the (COO) oxygens.<sup>45-50</sup> In complexes prepared under nonaqueous conditions picolinic acid N-oxide ligands are supposed to coordinate unidentately through their N-O oxygen, too.<sup>45</sup> Tridentate coordination through all the oxygens of picolinic acid N-oxide is believed to exist in the lanthanoid metal complexes.<sup>47</sup> Unidentate coordination through the N-O oxygen atom tends to be more common in the complexes of metal perchlorates prepared in ethanol - teof mixture.<sup>50</sup>

Nicotinic acid N-oxide is believed to coordinate

with divalent 3d metal ions mainly through the N=O oxygen and one of the (COO) oxygen atoms forming polynuclear polymeric compounds.<sup>3,54,55,57</sup> It can coordinate bidentately to adjacent metal ions through both carboxylate oxygen atoms, too.<sup>3</sup> There is, however, some suggestion that unidentate coordination occurs also through one of the (COO) oxygen atoms<sup>52</sup> or through the N=O oxygen.<sup>56,61</sup>

In metal complexes of isonicotinic acid N-oxide, ligands are expected to act mainly as bridging ligands coordinating bidentately through the N=O oxygen and one of the (COO) oxygen atoms.<sup>63,64</sup> In some complexes prepared in ethanol - toluene mixtures, ligands coordinated not only bidentately but also unidentately, and even tridentately, have been found.<sup>55-57</sup> All three pyridine monocarboxylic acid N-oxides are coordinated with  $UCl_4$  unidentately through the N=O oxygen in acidic conditions.<sup>61</sup>



## EXPERIMENTAL

## 1. Preparation of the compounds

The complexes of 3d metals ( $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ ) with picolinic acid N-oxide and isonicotinic acid N-oxide were synthesized in aqueous solutions. All metal salts were of pro analysi grade or better. Picolinic acid N-oxide (Aldrich Chemical Company, 97 %), and isonicotinic acid N-oxide (EGA-Chemie, 99 %), were used without further purification. In all syntheses the metal - ligand mole ratio was 1:1 or 1:2.

The original purpose of this work was to try to involve an inorganic anion in the structure by using different metal salts, but success was achieved with only one compound. Some syntheses were performed in anhydrous conditions with ethanol - toef mixture as solvent, but the result was a power-like and very insoluble compound, not suitable for X-ray work.

## 1.1. Metal complexes of picolinic acid N-oxide

All metal complexes of picolinic acid N-oxide were prepared according to instructions given in the literature<sup>45,50</sup> except that solutions were more dilute.

The iron(II) ion did not form a crystalline compound with picolinic acid N-oxide by this method because of

the easy oxidation of the Fe(II) ion in the water solution.

## 1.2. Metal compounds of isonicotinic acid N-oxide

Isonicotinic acid N-oxide dissolved in water by adding  $\text{NH}_3(\text{aq})$  and the excess  $\text{NH}_3$  removed by boiling.<sup>63</sup> This procedure was the same in every synthesis. The ammonium isonicotinate N-oxide solution was allowed to react with a suitable metal salt.

### 1.2.1. $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$

The hot solutions of  $\text{N-inicONH}_4$  and  $\text{Mn(II)}$  acetate were combined and a part of the  $\text{N-inicOH}$  that crystallized upon cooling was filtered off. The filtrate was evaporated nearly to dryness so that a thick syrup was left. This residue was then dissolved in ethanol - methanol (1:1) mixture from which almost colourless  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$  crystals formed.

### 1.2.2. $\text{M}(\text{N-inicO})_2(\text{H}_2\text{O})_6$ , $\text{M}=\text{Fe}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$

$\text{Co(II)}$  and  $\text{Ni(II)}$  acetates and  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were used as metal ion sources. The cobalt and nickel compounds crystallized upon cooling and the corresponding iron(II) compound crystallized after about two grams of  $\text{NaAc}$  was added to the hot solution to raise the pH-value.

1.2.3.  $\text{Cu}(\text{N-inoicO})_2(\text{H}_2\text{O})_2$ 

$\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$  was dissolved in cold water and after addition of ammonium isonicotinate N-oxide solution the mixture was kept hot for about half an hour. Crystallization occurred upon cooling.

1.2.4.  $\text{Cu}_4(\text{N-inoicO})_4(\text{OH})_2\text{SO}_4 \cdot (\text{H}_2\text{O})_4$ 

The hot solutions containing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and ammonium isonicotinate N-oxide were combined and filtered. About two grams of NaAc was added to the filtrate, causing immediate precipitation. Closer inspection of the precipitate revealed two different kinds of crystals. The green crystals were shown to be  $\text{Cu}_4(\text{N-inoicO})_4\text{SO}_4 \cdot (\text{OH})_2(\text{H}_2\text{O})_4$  and the blue ones  $\text{Cu}(\text{N-inoicO})_2(\text{H}_2\text{O})_2$ .

## 2. Analytical data

The analytical data of the metal complexes with isonicotinic acid N-oxide are presented in Table 1. The metals were determined by standard EDTA titrations, except in some cases where a Perkin-Elmer 5000 ICP spectrometer was used instead. The chemical analyses for C, N and H were performed by the Finnish Pulp and Paper Research Institute, in Espoo.

Table 1. Analytical data.

Compound	% M		% H		% C		% N	
	calc.	found.	calc.	found.	calc.	found.	calc.	found.
$\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$	13.63	13.39*	4.00	4.19	35.75	35.60	6.95	6.84
$\text{Fe}(\text{N-inicO})_2(\text{H}_2\text{O})_6$	12.69	11.65*	4.58	4.64	32.75	32.34	6.37	6.29
$\text{Co}(\text{N-inicO})_2(\text{H}_2\text{O})_6$	13.36	13.10	4.57	4.56	32.66	32.46	6.35	6.35
$\text{Ni}(\text{N-inicO})_2(\text{H}_2\text{O})_6$	13.31	13.09	4.57	4.54	32.68	32.41	6.35	6.40
$\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2$	16.91	16.60	3.22	3.16	38.36	38.28	7.45	7.54
$\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{OH})_2$ $(\text{H}_2\text{O})_4$	25.20	24.53	2.60	2.62	28.58	28.24	5.55	5.54

\*Determined by Perkin-Elmer ICP 5000 spectrometer

### 3. Infrared spectra

The IR-spectra were recorded on a Perkin-Elmer 283 infrared spectrometer in the region  $4000 - 200 \text{ cm}^{-1}$ . The KBr pellet technique was employed and the sample/KBr weight ratio was 1:200.

### 4. Data collection

The intensity data were collected with a SYNTEX P2<sub>1</sub> diffractometer. The diffraction equipment consisted of a Eulerian cradle four-circle goniometer manufactured by Syntex, a high voltage generator manufactured by Seifert & Co, a Data General Nova 1200 computer with 8 K of 16 bit word memory, a Pertec read/write tape station and a Texas Instruments heat printer.

The data were collected with the 0:20 data collection program, using variable scan rate  $1 - 15^\circ/\text{min}$ . One or two check reflections were recorded after every 50 - 100 reflections to test the stability of the crystal and the instrument. The diffractometer recentered the crystal after every 500 reflections.<sup>65</sup> No crystal studied in this work was damaged by the X-rays, and the stability of the high voltage generator was satisfactory. Graphite monochromatized  $\text{MoK}_\alpha$ -radiation ( $0.71069 \text{ \AA}$ ) was used for data collection.

The parameters for the primitive cell were determined

by selecting 10 - 15 suitable reflections from the Polaroid picture and refining with the Syntex centering program. The correctness of the unit cell solution given by the autoindexing program was confirmed by axial photographs. The subsequent fast data collection was carried out using the  $2\theta$  range  $15 - 30^\circ$ , and of the collected reflections 15 were selected for more accurate determination of the unit cell and the orientation matrix.

#### 5. Structure determinations

The h,k,l values, intensity and the standard deviation of the intensity were read from the Syntex data tape into the memory of a UNIVAC 1100/60 computer for further handling. The reading program rejected a reflex if  $I < 3\sigma(I)$ . The Lorentz and polarisation corrections were made with the DATRDN program of the XRAY 76 program package.<sup>66</sup> No corrections were made for absorption effects. The intensity file was modified for the MULTAN programs<sup>67,68</sup> to  $F_{\text{obs}}$  form by the NORMSF and MULDMP programs of the XRAY 76 system.

The space groups were tentatively determined from systematic absences of reflections in the fast precollection. The systematic absences in the final data collection later confirmed these space groups. The absences were clear for all structures and there were no difficulties in

determining the space group. Where space groups were not uniquely defined by the absences, structures were determined in all possible space groups by the MULTAN program package and the one that appeared most reasonable chemically was selected. Preference was given to the centrosymmetric space group.

The structure of  $\text{Co}(\text{N-picO})_2(\text{H}_2\text{O})_2$  was determined by the MULTAN78<sup>67</sup> program package, which gave the coordinates of all non-hydrogen atoms. Refinements and all other calculations were performed with the XRAY 76 programs.<sup>66</sup> After several block-diagonal refinement cycles with isotropic and anisotropic temperature factors for non-hydrogen atoms, the difference Fourier map gave the coordinates of the hydrogen atoms. The hydrogen atoms were then refined with isotropic temperature factors.

The structure of  $\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2$  was initially solved with MULTAN78<sup>67</sup> in the space group  $\underline{P1}$ , but when the molecule showed itself to be centrosymmetric it was removed to the origin and final refinement was carried out in the space group  $\underline{P\bar{1}}$ .

The structure of  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$  was solved by the MULTAN80<sup>68</sup> package and gave chemically reasonable solution in the space group  $\underline{Cc}$ . Later an attempt was made to refine the structure in the centric space group  $\underline{C2/c}$  by locating the central metal at the special

position  $(0, y, 3/4)$ . After calculating and refining the whole molecule the final  $R$  value was 0.047.

On the basis of the solved structures of picolinic acid N-oxide complexes the structure of  $\text{Co}(\text{N-inoicO})_2 \cdot (\text{H}_2\text{O})_6$  was assumed to be centrosymmetric and mononuclear, and because  $Z = 2$  the central metal was situated at the special position of the space group  $P2_1/c$ . The difference Fourier map gave the coordinates of all other atoms. The coordinates of the atoms of the  $\text{Co}(\text{N-inoicO})_2(\text{H}_2\text{O})_6$  compound were used in refining the other structures of this isomorphic series.

The MULTAN78 programs gave in the space group  $C2$  the coordinates of two copper ions, two oxygen atoms and one sulfur atom of  $\text{Cu}_4(\text{N-inoicO})_4(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_4$ . These coordinates were refined and the difference Fourier map gave the positions of all other non-hydrogen atoms. The determining of the hydrogen atoms was unsuccessful because the difference Fourier map showed two peaks ( $3.7$  and  $3.2 \text{ e}\text{\AA}^{-3}$ ) with no chemical meaning very close to the copper ions ( $0.5 \text{ \AA}$ ).

This procedure of determining the coordinates of the hydrogen atoms from the difference Fourier map does not give the true coordinates of the nuclei since the X-rays are scattered by the electrons. Hence the reported bond distances from hydrogen atoms to other atoms are too short. This appears especially in the bonding distances



of the coordinated water molecules.

In the structure factor calculations for all structures, the scattering factors for non-hydrogen atoms were those of Cromer and Mann<sup>69</sup> and for hydrogen atoms those of Stewart, Davidson and Simpson.<sup>70</sup> Crystal data for the solved structures are tabulated in Table 2.

All drawings were made with the local modified ORTEP II program.<sup>71</sup> In these drawings the ellipsoids do not indicate the atomic thermal motion but only atom locations.

Table 2. Crystal data for the picolinic acid and isonicotinic acid N-oxide metal compounds determined in this study.

Compound	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	V(Å <sup>3</sup> )	D <sub>o</sub> (gcm <sup>-3</sup> )	D <sub>c</sub>	Z	Space group	$\lambda$ MoK $_{\alpha}$ (cm <sup>-1</sup> )	Ref	R used
Mn(N-picO) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	6.682(2)	15.812(4)	7.006(3)	90	114.15(2)	90	675.4(3)			2	P2 <sub>1</sub> /c		1307	.033
Co(N-picO) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	6.673(3)	15.729(13)	6.993(2)	90	115.29(3)	90	663.6(6)	1.82	1.98	2	P2 <sub>1</sub> /c		1324	.030
Ni(N-picO) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	6.618(3)	15.713(10)	6.930(2)	90	115.38(3)	90	651.0(5)			2	P2 <sub>1</sub> /c		1076	.049
Cu(N-picO) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	6.634(11)	7.302(14)	7.968(9)	80.5(1)	89.4(1)	61.4(1)	333.1(9)	1.83	1.87	1	P1		1925	.039
Mn(N-inicO) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	19.343(6)	7.029(2)	11.640(4)	90	99.95(3)	90	1558.8(9)	1.68	1.72	4	C2/c	9.5	1174	.047
Fe(N-inicO) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	7.746(3)	9.877(5)	11.515(7)	90	91.77(3)	90	880.6(7)	1.60	1.66	2	P2 <sub>1</sub> /c	9.9	854	.043
Co(N-inicO) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	7.747(2)	9.326(2)	11.474(2)	90	91.08(2)	90	873.2(3)	1.60	1.68	2	P2 <sub>1</sub> /c	11.0	1427	.045
Ni(N-inicO) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	7.765(2)	9.725(6)	11.363(6)	90	91.20(3)	90	857.9(7)	1.68	1.71	2	P2 <sub>1</sub> /c	12.0	1295	.045
Cu <sub>4</sub> (N-inicO) <sub>4</sub> (OH) <sub>2</sub> SO <sub>4</sub> (H <sub>2</sub> O) <sub>4</sub>	19.809(8)	6.844(3)	19.533(12)	90	140.88(3)	90	1670(2)	1.99	2.01	2	C2	27.8	1499	.061

## RESULTS AND DISCUSSION

## 1. The metal complexes of picolinic acid N-oxide

1.1. Description of the structures of  $M(\text{N-picO})_2(\text{H}_2\text{O})_2$ ,  
M =  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ 

The  $\text{Mn}^{2+}$ -,  $\text{Co}^{2+}$ - and  $\text{Ni}^{2+}$ -complexes of picolinic acid N-oxide are isomorphic, they crystallize in the space group  $\underline{P}2_1/c$ , and the metal ion is situated at the special position. The Cu-complex differs from the isomorphic series in belonging to space group  $\underline{P}\bar{1}$ . In all four complexes the coordination occurs through the N-O oxygen and one of the (COO) oxygens<sup>45,46,50</sup> as was proposed, on the basis of spectral and magnetic features in the literature cited above (sects. 5.1. and 6.).

The molecular structures of bis(picolinato N-oxido) diaquomanganese(II), -cobalt(II) and -nickel(II) and the labeling of the atoms are shown in Fig. 1, and the packing scheme of the molecules is in Fig. 2. The structure of bis(picolinato N-oxido) diaquacopper(II) with the atomic labeling is shown in Fig. 3; the molecular packing is presented in Fig. 4. The coordination geometry of the central metal ion in the Mn-, Co- and Ni-complexes is slightly distorted octahedron, and in the Cu-complex is an elongated octahedron. In this

latter case, the Jahn-Teller effect causes an extension of the Cu-O<sub>w</sub> bond to 2.488(5) Å, which in the other complexes is between 2.094(3) and 2.226(1) Å. The most important bond distances and bond angles of the picolinate N-oxido complexes are presented in Table 3. The bond distances between the metal ions and the organic ligand oxygens range from 2.154(1) to 1.922(3) Å in order of decreasing metal-ion radius. The M-O4 bond distance becomes shorter, too, on moving from the Mn-complex to the Ni-complex (2.226(1) - 2.094(3)). The M-O4 distance of the Cu-complex deviates from this trend.

The change of the central coordinating metal has only a slight influence on the bond distances in the picolinate N-oxide ligand. The bond distances N1-O1 vary from 1.337(1) Å to 1.322(1) Å, whereas the same distance is 1.329(1) Å in the "free" nicotinic acid N-oxide.<sup>72</sup> The bond distance between the coordinated oxygen and the carbon atom, O2-C6, varies between 1.252(1) and 1.266(1) Å, and the uncoordinated oxygen carbon distance O3-C6 varies between 1.229(1) and 1.247(1) Å in the carboxylato group of the complexes. The corresponding distances in the free acid are 1.301(1) and 1.198(1) Å.<sup>72</sup> The angle of the carboxylato group, O2-C6-O3, is 125.3(1) - 123.1(4)°, compared with 125.15(4)° in the free acid.<sup>72</sup> Thus coordination does not cause any noticeable opening of the carboxylato group angle.

The hydrogen bonds connecting the molecules with each other through the aqua oxygen atom, O<sub>4</sub>, and the uncoordinated carboxylate oxygen atom, O<sub>3</sub>, are shown in Table 4. The hydrogen bonds are so oriented that one connects the molecules in the direction of the a axis and the other in the direction of the b axis. In the Mn - Ni complex series there is also a diagonal hydrogen bond in the ab plane (Figs. 2 and 4). The bond distances between the hydrogen and carbon or oxygen atoms vary from 0.5 to 1.1 Å with the shortest values in the coordinated water molecule (Table 4)(see p. 24).

Table 3. The bond distances (Å) and most important bond angles(°) with their standard deviations for  $M(N\text{-picO})_2(H_2O)_2$ ,  $M = Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ .

	Mn <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>
M-01	2.154(1)	2.061(1)	2.035(3)	1.947(4)
M-02	2.113(1)	2.079(1)	2.015(3)	1.922(3)
M-04	2.226(1)	2.148(1)	2.094(3)	2.488(5)
O1-N1	1.322(1)	1.341(1)	1.329(5)	1.330(2)
O2-C6	1.252(1)	1.274(1)	1.249(4)	1.266(2)
O3-C6	1.246(1)	1.271(1)	1.232(4)	1.229(2)
C6-C1	1.512(1)	1.507(2)	1.510(6)	1.500(2)
O1-M-02	97.17(3)	94.03(3)	92.3(1)	90.19(9)
O1-M-04	89.50(4)	89.99(5)	90.1(1)	87.1(2)
O2-M-04	88.79(3)	87.43(3)	88.1(1)	92.8(1)
N1-O1-M	120.88(6)	120.18(6)	118.6(3)	116.1(1)
C6-O2-M	128.43(6)	125.94(7)	126.2(3)	124.93(6)
O2-C6-O3	125.31(8)	124.41(9)	123.1(4)	124.77(9)

According to earlier X-ray structure determinations of pyridine N-oxide metal complexes, the angle N-O-M varies between  $116.7^\circ$  and  $134^\circ$  when the central metal ion is Fe(II),<sup>31</sup> Co(II),<sup>31,32,41</sup> Ni(II)<sup>30,39</sup> or Cu(II).<sup>28,31,33,38,40</sup> In present work the same angle varies from  $116.1(1)^\circ$  to  $120.88(6)^\circ$ . As in the published pyridine N-oxide complexes, the angle N-O-M is smallest for the copper complexes. If it is assumed that the N-oxide oxygen uses its  $sp^2$  orbitals for bonding with the nitrogen and the metal atom, and the N-O bond is pure double bond, then the theoretical M-O-N angle must be  $120^\circ$ .

Table 4. The hydrogen bonding data of  $M(N\text{-picO})_2(H_2O)_2$ , when  $M = Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$ .

	$Mn^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	
04-H5	.51(1)	.78(2)	1.0(1)	.74(1)	
04-H6	.93(1)	.86(1)	.95(4)	.66(1)	
* 04..03	2.729(1)	2.788(1)	2.737(3)	2.768(5)	i
** 04..03	2.751(1)	2.745(1)	2.736(5)	2.834(6)	ii
03..H6	2.36(1)	1.97(1)	1.80(4)	2.215(8)	
03..H5	2.26(1)	1.97(2)	1.71(7)	2.051(8)	
*** <04-H5-03	167(2)	175(1)	172(5)	163.5(6)	i
**** <04-H6-03	165(1)	160(1)	172(5)	156.9(7)	i

Symmetry operation code:

* $-x, 1/2-y, -z$	i $1/2-x, -y, -z$
** $x, y, z$	ii $x, y-1/2, z$
*** $1/2-x, 1/2-y, -z$	(for Cu-complex)
**** $1/2-x, 1/4+y, 1/4+z$	

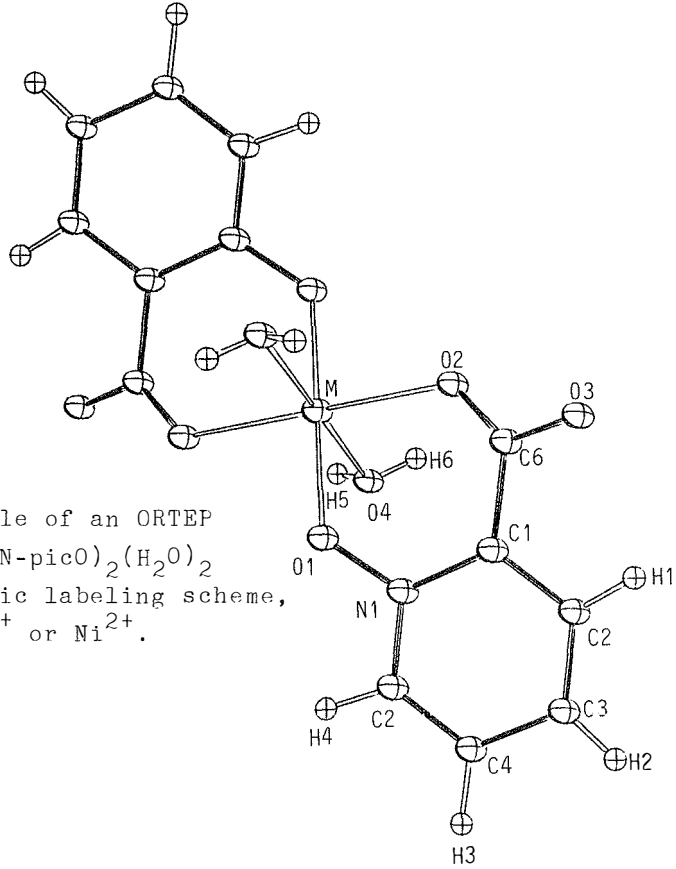


Fig. 1. Example of an ORTEP drawing of  $M(N\text{-picO})_2(H_2O)_2$  including atomic labeling scheme,  $M = Mn^{2+}$ ,  $Co^{2+}$  or  $Ni^{2+}$ .

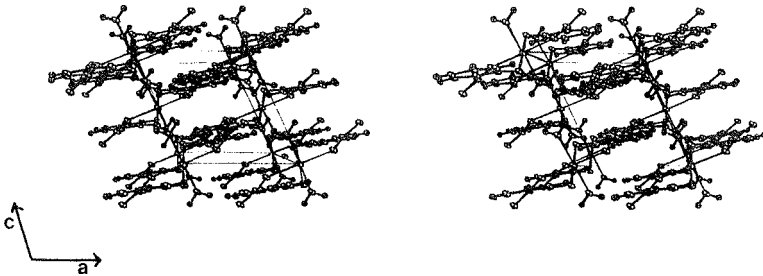


Fig. 2. A stereoview of the packing of  $M(N\text{-picO})_2(H_2O)_2$  in the unit cell.

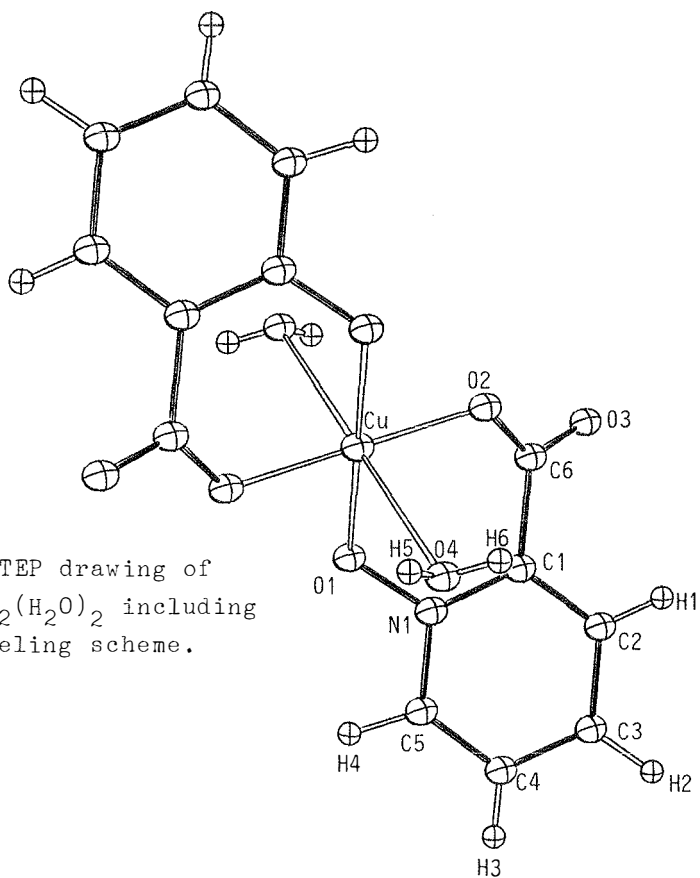


Fig. 3. ORTEP drawing of  $\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2$  including atomic labeling scheme.

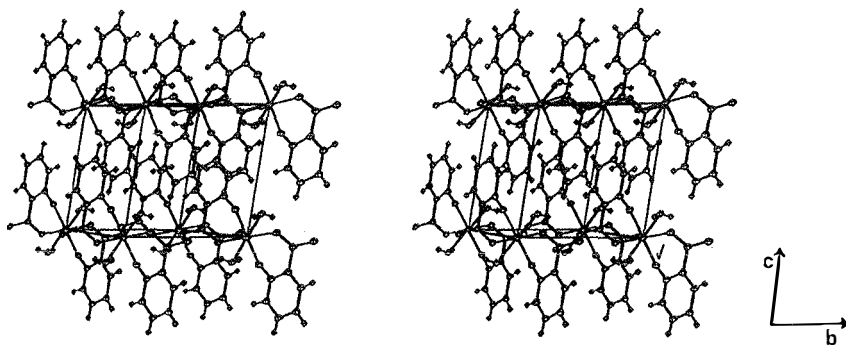


Fig. 4. A stereoview of the packing of  $\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2$  in the unit cell.



## 2. The metal compounds of isonicotinic acid N-oxide

### 2.1. Description of the structure of $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$

The systematic absences indicate two possible space groups; the centric  $C2/c$  and the acentric  $Cc$ . The structure was refined in both space groups to about the same  $R$ -value but the centric space group was selected because the sites of hydrogen atoms were more satisfactory.

The Mn central metal ion is situated at the special positions  $(0, y, 3/4)$ . Isonicotinic acid N-oxide acts as a unidentate ligand, coordinating only through one of its (COO) oxygen atoms to the central metal ion. A view and the atomic numbering of the molecule are shown in Fig. 5 and the packing of the complex in the unit cell appears in Fig. 6.

Gelfand et al. have synthesized a compound with the formula  $\text{Mn}(\text{N-inicO})_2 \cdot 5\text{H}_2\text{O}$ . They have predicted that the isonicotinic acid N-oxide coordinates through the N=O oxygen and one of the (COO) oxygens acting as a bridging ligand between metal ions. Two water molecules are assumed to coordinate to the manganese ion, while the rest are lattice waters.<sup>63</sup>

The coordination of the metal ion in  $\text{Mn}(\text{N-inicO})_2 \cdot (\text{H}_2\text{O})_4$  is trans octahedral. There are four oxygen atoms ( $04, 04'$  and  $05, 05'$ ) in the basal plane, with bond

distances of 2.201(3) and 2.172(4) Å, respectively. At the apical points of the octahedron are two water oxygens (O2, O2'), the bonding distance being 2.119(3) Å. The atoms O5, O5', O2, O2' and Mn define the basal plane of the coordination octahedron and the standard deviation of the oxygen atoms from this plane is about 0.018 Å. The apical bond Mn-O2 forms an angle of 176.1° with the basal plane. The coordination octahedron is compressed at the apical distance.

The trans-bis(isonicotinato N-oxide)tetraaqua-manganese(II) molecules form chains in the direction of the a axis of the unit cell. These chains are connected together by the hydrogen bonds between N-O oxygens, uncoordinated (COO) oxygens and the aqua ligands (Table 5). The N-O oxygen atom O1 form hydrogen bonds with the aqua ligands of the neighbouring molecules. These hydrogen bonds vary from 2.706(4) to 2.784(5) Å. There are also other hydrogen bonds with coordinated water molecules and the uncoordinated carboxylate oxygen O3. Intramolecular hydrogen bonds between coordinated water molecules are unlikely, because water molecules are rather far from one another and the O-H-O angle is too small.

Table 6 presents some of the most important bonding distances and angles with standard deviations.

The coordination sphere of the manganese(II) ion is

what would be expected on the basis of the  $\text{Mn}(\text{N-picO})_2 \cdot (\text{H}_2\text{O})_2$  complex already described and the complexes  $[\mu\text{-(acetato-0,0)}] \text{bis-}[\mu\text{-(acetato-0,0')}] (\text{acetato-0}) \text{diaqua-dimanganese(II)hexahydrate}^{15}$  and  $\text{bis}(\mu\text{-formato-0,0}) \text{bis}(\text{formato-0}) \text{tetraaquadimanganese(II)}^{73}$  presented in the literature. The Mn-O bond distances in all these compounds are of the same magnitude, 2.28 - 2.11 Å.

The bond distances C4-O3 and C4-O2 in the coordinated isonicotinate N-oxide ligand are 1.232(5) and 1.248(6) Å, respectively, and compare well with the corresponding distances found in picolinic acid N-oxide complexes. The angle of the carboxylato group, O2-C4-O3, is 127.7(4)°. A slight opening of the carboxylato group can be observed. The N-O bond distance is 1.325(4) Å and this value is quite normal.

Table 5. The hydrogen bonds (Å) of  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$ .

A-H...B	A-H	H...B	A-B	$\angle \text{AHB}^\circ$
O4-H5...O1	.88(5)	1.87(5)	2.706(4)	158(6) *
O4-H6...O1	1.01(7)	1.76(7)	2.752(5)	165(6) **
O5-H7...O1	.77(5)	2.03(5)	2.784(5)	165(6) ***
O5-H8...O3	.84(7)	1.87(7)	2.698(4)	174(8) ****

\*-1/2+x, 1/2+y, z

\*\*1/2-x, 1/2-y, 1-z

\*\*\*1/2-x, 1/2-y, 1-z

\*\*\*\*1/2-x, 1/2+y, 1/2-z

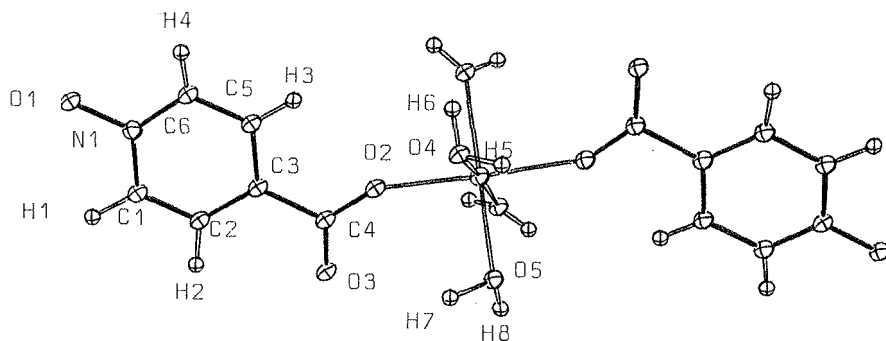


Fig. 5. An ORTEP drawing of the  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$  molecule including atomic labeling scheme.

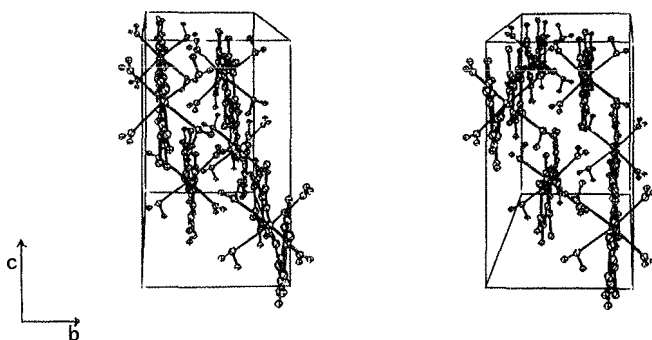


Fig. 6. Stereoscopic view of the unit cell of  $\text{Mn}(\text{N-inicO})_2 \cdot (\text{H}_2\text{O})_4$ .

Table 6. Selected bonds (Å) and angles (°) with standard deviations in  $\text{Mn}(\text{N-isonicotinate})_2(\text{H}_2\text{O})_4$ .

Bond		Angle	
Mn-O2	2.119(3)	O2-Mn-O2'	176.3(2)
Mn-O4	2.201(3)	O4-Mn-O5	173.9(1)
Mn-O5	2.172(4)	O4-Mn-O5'	95.0(1)
C4-O2	1.248(6)	O4-Mn-O4'	79.1(1)
C4-O3	1.232(5)	Mn-O2-C4	153.1(3)
C3-C4	1.522(5)	O2-C4-O3	127.7(4)
N1-O1	1.325(4)	H5-O4-H6	101(5)
C1-H1	1.04(4)	H7-O5-H8	120(6)
C2-H2	.97(4)		
C5-H3	.98(5)		
C6-H4	.91(4)		
O4-H5	.88(5)		
O4-H6	1.01(7)		
O5-H7	.77(5)		
O5-H8	.84(7)		

2.2. Description of the structures of  $\text{M}(\text{N-isonicotinate})_2(\text{H}_2\text{O})_6$ ,  
 $\text{M} = \text{Fe}^{2+}, \text{Co}^{2+}$  and  $\text{Ni}^{2+}$

Hexaaquairon(II), -cobalt(II) and -nickel(II) di-isonicotinate N-oxide are ionic compounds comprising the metal hexaaqua cation and isonicotinate N-oxide anions. The structures form an isomorphic series. The same isomorphism was observed for the Mn(II), Co(II) and Ni(II) complexes of picolinic acid N-oxide.

The interatomic bond distances and angles with standard deviations are given in Table 7. A view and

numbering of the atoms is shown in Fig. 7 and an example of the packing of the ions in Fig. 8.

The metal ions are situated at the special positions of the space group  $P2_1/c$  and are coordinated octahedrally by six water molecules. The geometry around the metal ions is almost undistorted. The  $M-O_w$  distances are 2.081(2) - 2.112(3) Å for Fe(II), 2.052(2) - 2.092(2) Å for Co(II) and 2.031(2) - 2.063(3) Å for Ni(II). These values compare well with the  $M-O_w$  distances in  $M(H_2O)_6^{2+}$  cations reported in the literature.<sup>19,20</sup> Isonicotinate N-oxide acts as anion in these structures. In the carboxylate groups the carbon - oxygen distances C6-O2 and C6-O3 are 1.087(8) and 1.430(9) Å for the Fe(II) compound, 1.249(4) and 1.246(3) Å for the Co(II) compound, and 1.260(5) and 1.248(5) Å for the Ni(II) compound. The deviation in the values of the Fe(II) compound indicates that the carboxylate group is disordered.

There is no direct coordination between the metal ion and the isonicotinate N-oxide ions. All distances between the metal ion and the three oxygens (O1, O2 and O3) of the isonicotinate N-oxide ion are greater than the contact distance 3.8 Å. The structure determination verified that the Fe, Co and Ni compounds are ionic, consisting of hexa-aquametal(II) cations and isonicotinate N-oxide anions. The ions are held together in the lattice by strong hydrogen bonds between the coordinated water molecules

and the oxygen atoms of the two anions. The hydrogen bonds listed in Table 8 are about 2.7 Å.

The oxygen atoms of the water octahedrons are quite close to each other. The distances are typical for hydrogen bonds, varying from about 2.9 to 3.1 Å in all studied complexes, but the actual existence of hydrogen bonds seems improbable since the oxygen - hydrogen - oxygen angles are not favourable.

Gelfand et al.<sup>63</sup> have proposed that compounds described above are polynuclear, with isonicotinate N-oxide coordinated through the N-O oxygen and one of the (COO) oxygens, acting as a bridging ligand between adjacent metal ions. Two water molecules were interputed as aqua ligands and four as lattice waters.

### 2.3. Description of the structure of di- $\mu_3$ -hydroxo- $\mu$ -sulfato tetrakis- $\mu$ -(isonicotinato N-oxide)tetraaqua tetracopper(II)

The labeling of the atoms in the molecule is shown in Fig. 9 and the molecular packing in the unit cell can be seen in Fig. 10. Some selected interatomic distances and angles with estimated standard deviations are given in Table 10.

All copper atoms have square pyramidal geometry. Cu1 coordinates with isonicotinate N-oxide through the

Table 7. Bond distances(Å) and angles( $^{\circ}$ ) with their standard deviations for  $M(N\text{-inicO})_2(H_2O)_6$ ,  $M = Fe^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$ .

Bond	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$
M-04	2.081(2)	2.070(2)	2.031(2)
M-05	2.112(2)	2.052(2)	2.033(2)
M-06	2.112(3)	2.092(2)	2.063(3)
O1-N1	1.327(4)	1.324(2)	1.319(3)
N1-C1	1.361(8)	1.328(5)	1.358(6)
N1-C4	1.321(8)	1.358(5)	1.342(6)
C1-C2	1.415(5)	1.383(4)	1.378(5)
C2-C5	1.251(14)	1.390(4)	1.395(5)
C5-C3	1.523(16)	1.373(4)	1.374(6)
C3-C4	1.361(5)	1.368(4)	1.375(5)
C5-C6	1.514(4)	1.505(3)	1.509(4)
C6-O2	1.087(8)	1.249(4)	1.260(5)
C6-O3	1.430(9)	1.246(3)	1.248(5)
O4-M-05	92.35(9)	92.68(7)	91.13(9)
O4-M-06	90.23(12)	90.11(8)	90.20(10)
O5-M-06	88.56(11)	88.85(7)	89.70(10)
O1-N1-C1	117.1(7)	118.6(3)	119.2(4)
O1-N1-C4	120.8(7)	120.4(3)	119.9(4)
C5-C6-O2	125.8(9)	117.2(3)	117.7(3)
C5-C6-O3	109.4(8)	117.8(3)	116.8(4)
O2-C6-O3	124.7(3)	125.0(3)	125.5(3)



Table 8. The hydrogen bonds (Å) of  $M(\text{N-inicO})_2(\text{H}_2\text{O})_6$ ,  
 $M = \text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ .

A-H····B	A-H	H····B	A-B	$\angle \text{AHB}^\circ$
$\text{Fe}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
06-H6····01	1.05(11)	1.95(8)	2.676(4)	126(13) *
05-H9····02	.90(4)	1.82(4)	2.662(3)	156(4) **
04-H8····03	.86(6)	1.84(6)	2.681(3)	165(6) ***
$\text{Co}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
06-H6····01	.94(3)	1.87(3)	2.639(2)	153(3) *
05-H9····02	.95(3)	1.80(3)	2.687(2)	156(3) **
04-H8····03	.99(3)	1.68(4)	2.667(2)	174(3) ***
$\text{Ni}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
06-H6····01	.65(3)	2.14(4)	2.667(4)	160(4) **
05-H9····02	.93(5)	1.77(5)	2.668(4)	162(4) **
04-H8····03	.73(5)	1.94(6)	2.673(3)	175(6) ***

\* x, y, z

\*\* x, y, 1/2+z

\*\*\* 1-x, 1-y, 1/2-z

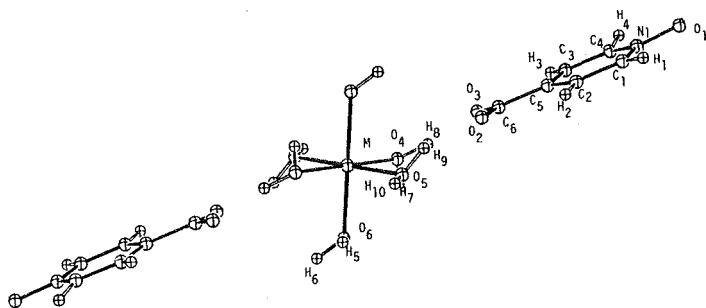


Fig. 7. Example of an ORTEP drawing of an  $M(N\text{-inicO})_2 \cdot (H_2O)_6$  including atomic labeling scheme.

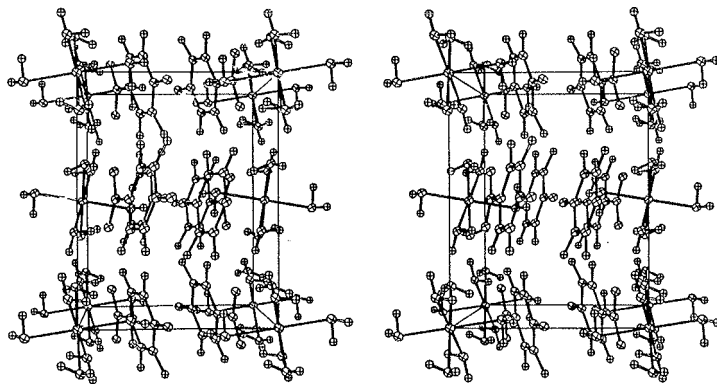
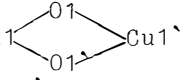


Fig. 8. A stereoview of the packing of  $M(N\text{-inicO})_2 \cdot (H_2O)_6$  in the unit cell; projection is on the  $ab$  plane.

carboxylate oxygens O2 and O5 and with  $\mu_3$ -bridging hydroxo oxygens O1 and O1' on the basal plane. Bond distances are 1.92(3) - 1.99(1) Å. These values compare well with the Cu-O distances in tetranuclear bis-[di- $\mu$ -(phenylmethoxy)-bis(pentane-2,4-dionato)dicopper(II)] (CuPhmP).<sup>74</sup> In the studied complex the axial Cu1-O8 distance is 1.98(4) Å, which is considerably shorter than the axial Cu-O distances of 2.42 and 2.71 Å in CuPhmP<sup>74</sup> and 2.15 Å in  $\mu_3$ -hydroxo-tri- $\mu$ -(pyridine-2-carbaldehyde oximato)- $\mu_3$ -sulfato tricopper(II) 16.3 water (CuPCAO).<sup>75,76</sup> Cu1 is clearly removed from the least-squares basal plane (standard deviation of the plane defining atoms is 0.005) towards the sulfato oxygens O8 and O8'; this deviation is 0.27 Å.

Cu2 has the  $\mu_3$ -hydroxo oxygen O1, carboxylate oxygens O6 and O3' and one water oxygen O11 in the basal coordination plane. The bond distances are 1.94(1) to 2.00(1) Å and correspond to the distances that Cu1 has in its basal plane. The apical distance Cu2-O10 is 2.17(1) Å and agrees with the above-noted value of 2.15 Å in CuPCAO.<sup>75,76</sup> 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. The literature contains descriptions of many compounds with the  $M_3O$ -core when the central metal is Fe(III), Cr(III) or Mn(III),<sup>77-81</sup> but only two systems involving the  $Cu_3O$ -core.<sup>75,76,82</sup>

In the present case two  $\mu_3$ -OH link the copper atoms together. The copper - hydroxo - oxygen bond distances are 1.94(1) - 1.99(1) Å and the Cu1-O1-Cu1' angle is 92.2(5)° and Cu2-O1-Cu1 angle 117(1)°. In the  $\mu_3$ -hydroxo (oxo)tri- $\mu$ -(2-propylamino-2-methyl-3-butanone oximate) triaquatrocopper(II) ion (CuPrAO)<sup>82</sup> the same angle is 108.2° and the Cu-O distances are 1.97 and 1.99 Å, respectively.

In the centre of the molecule there is a Cu1  Cu1' four-membered ring. The angles O1'-Cu1-O1 and Cu1'-O1-Cu1 are 82.3(7)° and 92.2(5)°, respectively. The ring is folded so that O1 and O1' lie under the Cu1 and Cu1' atoms. The Cu1-Cu1' distance of 2.855(6) Å is quite short, but not the shortest known, e.g.<sup>3,83,87</sup>

The sulfur of the sulfate group is situated at the special position on the twofold axis. Sulfate ion forms a bidentate bridge between Cu1 and Cu1'. The Cu-O distance to the sulfate oxygen O8 is 1.98(4) Å, which is considerably shorter than the same distance 2.15 Å in the CuPCAO complex.<sup>75,76</sup> The oxygens O9 and O9' of the sulfate group form intermolecular hydrogen bonds with the  $\mu_3$ -hydroxo oxygens O1 and O1' of the second molecule. Data for proposed hydrogen bonds are given in Table 9.

Isonicotinate N-oxide acts as a bridging ligand, coordinating with Cu1 and Cu2 through both of its (C00) oxygens. The Cu-O bond distances are from 1.92(1) to

1.97(2) Å. In the carboxylate groups the carbon - oxygen distances vary from 1.23(4) to 1.27(3) Å and are normal values. The angles of the carboxylate groups are 125(3)<sup>o</sup> and 129(3)<sup>o</sup> and of the same magnitude as in the other compounds determined in this work. The N-O distances are 1.30(4) and 1.32(3) Å and also quite normal. The N-oxide oxygens do not coordinate with the copper atoms, but they take part in intermolecular hydrogen bonds with the aqua ligands (O10 and O11).

Table 9. The hydrogen bonds in  $\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{OH})_2 \cdot (\text{H}_2\text{O})_4$ .

Bond	(Å)	Symm. operation
04.....010	2.69(3)	$x+1/2, y+1/2, z$
04.....011	2.63(3)	$x+1/2, y-1/2, z$
07.....010	2.76(3)	$x, 1+y, z$
07.....011	2.67(3)	$x, y, z$
01.....09	2.51(3)	$x+1/2, y-1/2, z$

Table 10. Some selected interatomic distances(Å) and angles( $^{\circ}$ ) with their standard deviations in  $\text{Cu}_4(\text{N-inoicO})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$ .

Bond		Angle	
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)
S1-O8	1.65(4)	O8-S1-O9	114.8(13)
S1-O9	1.50(2)	O9-S1-O9`	104.5(13)
O2-C6	1.26(2)	C9-C10	1.42(2)
O3-C6	1.24(3)	C8-C7	1.39(3)
C6-C3	1.46(5)	C10-C11	1.39(4)
C3-C2	1.40(3)	C7-N2	1.33(4)
C3-C4	1.42(3)	C11-N2	1.37(2)
C2-C1	1.35(5)	N2-O7	1.32(3)
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)		

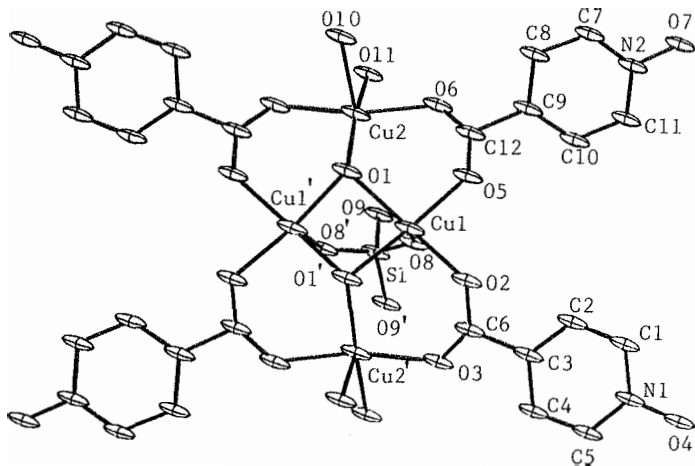


Fig. 9. An ORTEP drawing of  $\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$  including the atomic labeling scheme.

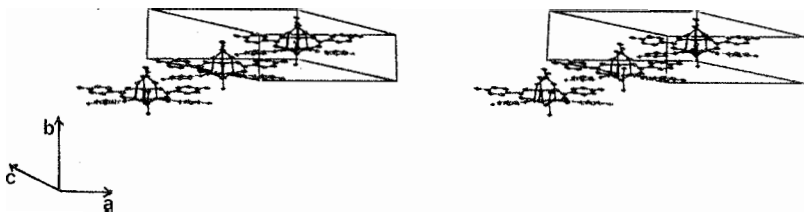


Fig. 10. A stereoview of partial packing of  $\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{H}_2\text{O})_4$  in the unit cell.

### 3. The IR-spectra

The spectra of the metal compounds of isonicotinic acid N-oxide are presented in Figs. 11 and 12, with the most important absorptions collected in Table 11.

#### 3.1. Absorptions of the carboxylic group

Four different coordinations of the carboxylic group appear in the solvated metal compounds of isonicotinic acid N-oxide: unidentate, syn-syn bridging bidentate, chelating ligand and ionic. The unidentate coordination could be expected to eliminate the similarity of the two carboxylic oxygen atoms by increasing the frequency of the  $\nu_{\text{asym}}$  (COO) vibration and decreasing that of  $\nu_{\text{sym}}$  (COO). The difference between these two frequencies should be larger than the difference for the corresponding "free" acid ion.<sup>88</sup> The frequencies in question in the unidentate  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$  complex are  $1665 \text{ cm}^{-1}$  and  $1370 \text{ cm}^{-1}$ , the difference  $\Delta$  being  $295 \text{ cm}^{-1}$ . In the ionic  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  compounds, the  $\nu_{\text{asym}}$  (COO) band lies between  $1665$  and  $1650 \text{ cm}^{-1}$ , the  $\nu_{\text{sym}}$  band between  $1382$  and  $1385 \text{ cm}^{-1}$  and  $\Delta$  range from  $286$  to  $265 \text{ cm}^{-1}$ , being largest for the Ni-complex and smallest for the Fe-complex. Clearly, the coordination of the carboxylic group can not easily be predicted from the magnitude of  $\Delta$ , at least in the present compounds.



The N-inicO ligand coordinates as a bidentate bridge in the  $\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$  complex. The frequency of  $\nu_{\text{asym}}(\text{COO})$  is  $1625 \text{ cm}^{-1}$  and  $\nu_{\text{sym}}(\text{COO})$   $1410 \text{ cm}^{-1}$ , while  $\Delta$  is  $215 \text{ cm}^{-1}$ . Once again expectations are not borne out, for would expect the frequencies of  $\nu(\text{COO})$  in the bidentate coordination to be close to the frequency values and  $\Delta$  value of the free ion.<sup>88</sup>

Although the diffractometric structure determination of bis(isonicotinato N-oxide)diaquacopper(II) has not yet been completed, (R=12%) the coordination of the N-inicO ligand in it is quite clear.<sup>89</sup> The isonicotinic acid N-oxide acts as a bidentate chelating ligand coordinating through both oxygen atoms of the carboxylic group with the same copper atom. In the chelate coordination the  $\nu_{\text{asym}}(\text{COO})$  frequency should decrease and the  $\nu_{\text{sym}}(\text{COO})$  frequency increase relative to the values of the free ion. Such a trend can be seen, but it is very slight.

At least one group of authors consider that the frequencies of the  $\nu(\text{COO})$  absorptions do not correlate with the structures in any other way except that a large  $\Delta$  value points to unidentate coordination.<sup>90</sup> The present work support this opinion.

### 3.2. Absorption of the N-O group

For the isonicotinic acid N-oxide the N-O stretching

absorption is at  $1290\text{ cm}^{-1}$  and the bending absorption at  $855\text{ cm}^{-1}$ . The N-O absorption is considered to move to lower frequency when coordination takes place through the N-O oxygen.<sup>45-50,63</sup> Such lowering of frequencies of the N-O absorptions occurs for the complexes of this work, too; the difference is  $75 - 59\text{ cm}^{-1}$  from the value  $1290\text{ cm}^{-1}$  of isonicotinic acid N-oxide, although the N-O oxygen atom does not take part in the coordination to the metal ion in any compound studied here.

Apparently the lowering is due to the strong hydrogen bonds in which the N-O oxygen atom participates.

### 3.3. Absorptions of the aqua ligands

The absorptions of the coordinated water molecules of the manganese and ionic iron, cobalt and nickel compounds appear in the same region of  $3300 - 3400\text{ cm}^{-1}$ .

In  $\text{Cu}_4(\text{N-inicO})_4(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_4$  the aqua ligand absorption appears as a strong peak at  $3310\text{ cm}^{-1}$ . In  $\text{Cu}(\text{N-inicO})_2(\text{H}_2\text{O})_2$  the water absorptions are one on top of each other, with the CH absorptions in the  $3100\text{ cm}^{-1}$  region.

The H-O-H bending mode appears in all complexes in the region  $1592 - 1620\text{ cm}^{-1}$ .

### 3.4. $\text{SO}_4^{2-}$ and $\text{OH}^-$ absorptions in $\text{Cu}_4(\text{N-isonico})_4(\text{OH})_2 \cdot \text{SO}_4(\text{H}_2\text{O})_4$

Because the  $T_d$ -symmetry of the sulfate group has been lowered due to its coordination to the  $C_{2v}$ , it is not possible to see a very strong  $\nu_3$  absorption band of sulfate in the spectra. The  $\nu_1$  and  $\nu_3$  absorption bands of the sulfato group are found in the region 1200 - 1000  $\text{cm}^{-1}$ . Absorptions of the isonicotinate N-oxide and the bridging OH groups appear in the same region, too. The bands close to 1050  $\text{cm}^{-1}$  may be due to the bridging OH bending mode. The wagging, rocking and metal - oxygen stretching modes of coordinated water are seen in the regions 600 - 900  $\text{cm}^{-1}$  together with the  $\nu_4$  absorption of sulfato group. These bands are very sensitive to the strength of the coordinate bonds, as well as to the hydrogen bonds in the crystals. The  $\nu_2$  absorption of sulfato is at about 450  $\text{cm}^{-1}$ .

Table 11. Infrared absorption bands due to (COO), coordinated water and N-O groups of isonicotinic acid N-oxide and its complexes ( $\text{cm}^{-1}$ ).

	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta$	Coordinated water		M-O wagging	$\nu(\text{NO})$	$\sigma(\text{NO})$
				$\nu(\text{OH})$	$\nu(\text{H-O-H})$	rocking, stretching		
N- <i>inico</i> H	1720	1440	280	3420*			1290	855
Mn(N- <i>inico</i> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	1665	1370	295	3400	1620	550 - 850	1225	860
Fe(N- <i>inico</i> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	1650	1385	265	3370	1592	530 - 820	1230	869
Co(N- <i>inico</i> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	1658	1385	273	3395	1599	542 - 822	1231	869
Ni(N- <i>inico</i> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub>	1668	1382	286	3390	1595	550 - 830	1230	860
Cu(N- <i>inico</i> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	1625	1375	250	3110	1620	530 - 830	1215	870
Cu <sub>4</sub> (N- <i>inico</i> ) <sub>4</sub> SO <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	1625	1410	215	3300	1610	600 - 900	1222	865

\* carboxyl hydroxo

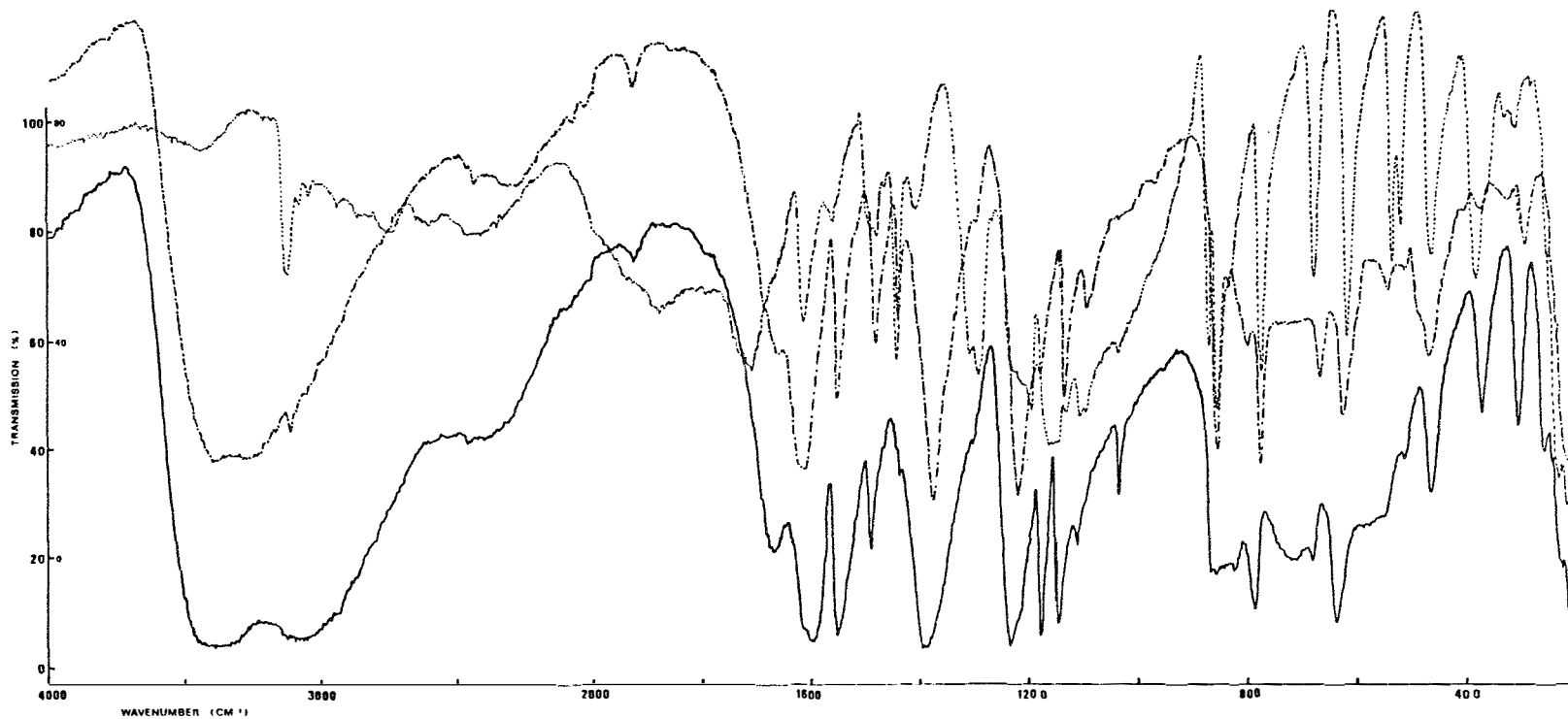


Fig. 11. Infrared spectra of isonicotinic acid N-oxide(.....), Ni(N-isonicotinate)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(——) and Mn(N-isonicotinate)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(-·-·-).

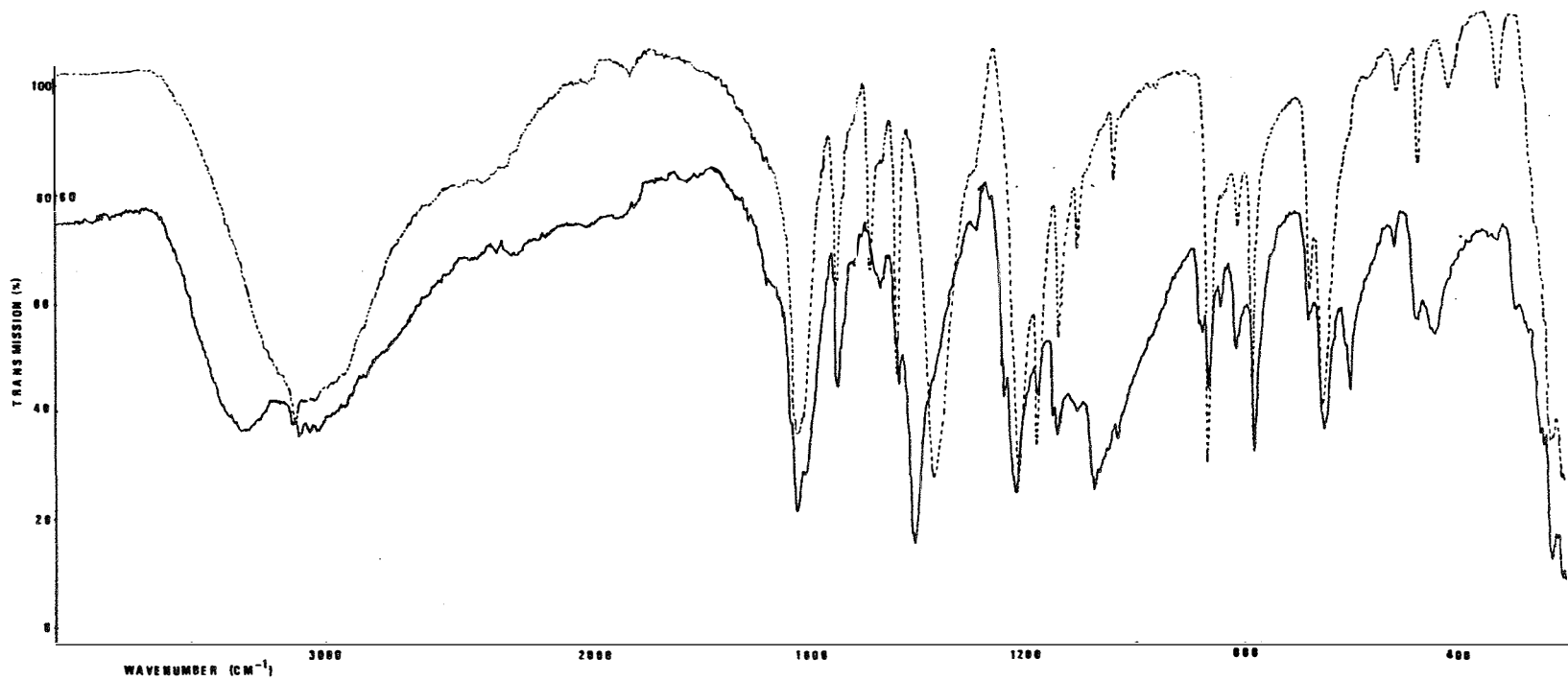


Fig. 12. Infrared spectra of  $\text{Cu}(\text{N-inico})_2(\text{H}_2\text{O})_2$  (---) and  $\text{Cu}_4(\text{N-inico})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$  (—).

## CONCLUSIONS

The metal complexes of picolinic acid N-oxide studied in this work form an isomorphous series, except for the copper complex, which differs probably owing to the Jahn-Teller distortion. In general, this study confirms results obtained previously on the coordination in these complexes.

The results on structures and coordination of the investigated isonicotinic acid N-oxide compounds  $Mn(N-inoicO)_2(H_2O)_4$ ,  $Fe(II)-$ ,  $Co(II)-$ ,  $Ni(II)(N-inoicO)_2 \cdot (H_2O)_6$  and  $Cu(N-inoicO)_2(H_2O)_2$ , synthesized in aqueous solution, are at variance with conclusions drawn earlier. The earlier results were based on the IR-spectra and the magnetic properties of the metal complexes of pyridine N-oxide and pyridine carboxylic acids.

Isonicotinic acid N-oxide can be attached to the central metal ion in different ways. Except in the ionic compounds, coordination occurs with the  $3d$  metal ions only through the carboxylic oxygen atoms. N-inoicO ligand coordinates with manganese(II) monodentately through one of the (COO) oxygens. Isonicotinate N-oxide can act as a bidentate ligand, coordinating through both of the carboxylic oxygen atoms to form a chelate ring as in  $Cu(N-inoicO)_2(H_2O)_2$ , or it can act as a bridge between two

separate metal ions as in  $\text{Cu}_4(\text{N-inoicO})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$ . N-inoicOH forms with iron(II), cobalt(II) and nickel(II) ions, ionic compounds in which the metal ion coordinates with six water molecules octahedrally, forming hexaaqua metal(II) cation; isonicotinate N-oxide acts as anion in the lattice. These compounds form an isomorphous series.

A new complex was isolated from the aqueous solution of isonicotinic acid N-oxide and Cu(II) sulfate pentahydrate. In this tetranuclear complex two copper ions are very close to each other in the molecule; the Cu-Cu distance is 2.86 Å. The coordination around the copper ions is square pyramidal with a rather long axial coordination. The isonicotinate N-oxide acts as a bridging ligand, coordinating bidentately through both of the carboxylate oxygen atoms and forming bridges between copper atoms. Two hydroxo groups form threefold bridges symmetrically between the copper atoms. The sulfate group forms a bridge between two copper atoms.



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APPENDIX

The anisotropic thermal parameters for non-hydrogen atoms for all the solved structures are of the form  $\exp(-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}))$ .

Table 12.  $\text{Mn}(\text{N-picO})_2(\text{H}_2\text{O})_2$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mn	.0000	.5000	.5000	11.58(7)	18.87(7)	23.95(8)	1.33(7)	2.83(6)	1.99(8)
O1	.90919(9)	.61570(4)	.32255(10)	17.5(3)	25.5(3)	39.5(3)	2.9(2)	13.1(3)	7.7(3)
O2	1.34338(9)	.51779(3)	.62314(9)	14.5(3)	21.5(3)	38.5(3)	-.4(2)	3.5(2)	5.7(2)
O3	.32470(9)	.50704(4)	.13018(9)	16.9(3)	28.3(3)	32.6(3)	-4.3(3)	-.5(2)	-.2(3)
O4	.00425(10)	.43197(4)	.22350(9)	21.3(3)	33.7(3)	30.0(3)	-.4(3)	8.4(3)	-1.1(3)
N1	.73912(11)	.66063(4)	.31496(10)	16.6(3)	20.1(3)	23.9(3)	-.6(3)	5.7(3)	2.5(3)
C1	.54090(13)	.62508(5)	.27754(12)	17.5(4)	20.8(4)	23.8(4)	-1.0(3)	6.1(3)	1.1(3)
C2	.36646(14)	.67665(6)	.25875(14)	22.6(4)	28.2(4)	32.5(4)	3.7(4)	11.2(4)	1.2(4)
C3	.39042(16)	.76344(6)	.27607(15)	35.5(5)	24.3(4)	40.6(5)	8.6(4)	18.5(4)	1.4(4)
C4	.59428(17)	.79760(5)	.31644(15)	43.8(6)	18.5(4)	39.8(5)	.3(4)	17.2(5)	-.8(4)
C5	.76534(15)	.74594(5)	.33407(14)	29.3(5)	21.2(4)	33.2(5)	-6.5(4)	9.4(4)	.6(3)
C6	.50856(13)	.53026(5)	.25941(13)	15.7(4)	21.8(4)	25.6(4)	-1.3(3)	8.9(3)	.7(3)

Table 13.  $\text{Co}(\text{N-picO})_2(\text{H}_2\text{O})_2$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	.0000	.5000	.5000	10.48(5)	21.2(1)	21.45(6)	1.24(7)	3.76(5)	2.80(7)
O1	.92226(9)	.61084(4)	.32999(9)	15.4(2)	29.2(4)	33.9(3)	4.0(2)	11.4(2)	7.6(2)
O2	1.33588(9)	.52275(4)	.62530(9)	12.3(2)	25.4(4)	35.2(3)	-.3(2)	3.9(2)	5.9(2)
O3	.32515(9)	.50590(4)	.13252(9)	15.5(2)	32.2(4)	30.4(3)	-2.1(3)	.8(2)	1.4(3)
O4	.00775(10)	.43432(4)	.23461(9)	19.2(3)	33.9(4)	26.4(3)	-.6(2)	7.7(2)	-.3(3)
N1	.75281(10)	.65806(5)	.32331(10)	16.1(3)	23.2(5)	21.2(3)	1.1(3)	5.5(2)	3.2(3)
C1	.55210(12)	.62254(6)	.28404(12)	17.1(3)	21.1(5)	21.0(3)	-.5(3)	6.5(3)	1.0(3)
C2	.37864(13)	.67638(6)	.26505(13)	20.6(4)	26.2(6)	31.5(4)	2.6(3)	10.3(3)	1.7(4)
C3	.40743(15)	.76336(7)	.28360(14)	32.3(5)	30.2(7)	33.9(4)	9.5(4)	15.6(4)	2.3(4)
C4	.61465(16)	.79700(6)	.32587(14)	40.5(5)	24.0(6)	34.1(4)	-.2(4)	15.6(2)	-.0(4)
C5	.78353(15)	.74283(6)	.34480(13)	26.9(4)	21.4(4)	28.8(4)	-5.9(4)	8.3(3)	1.5(3)
C6	.51522(12)	.52834(6)	.26183(12)	14.5(3)	28.0(6)	20.8(3)	-2.1(3)	7.3(3)	1.5(3)

Table 14. Ni(N-picO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Ni	.0000	.5000	.5000	13.7(3)	20.6(3)	21.1(3)	.3(3)	5.5(2)	2.6(3)
O1	.9296(4)	.6108(2)	.3319(4)	21(1)	27(2)	34(1)	4(1)	14(1)	9(1)
O2	1.3317(5)	.5224(2)	.6275(4)	21(1)	24(2)	34(1)	1(1)	9(1)	6(1)
O3	.3268(4)	.5067(2)	.1338(4)	20(1)	28(2)	30(1)	0(1)	4(1)	2(1)
O4	.0091(5)	.4362(2)	.2386(4)	22(1)	34(2)	25(1)	0(1)	12(1)	0(1)
N1	.7589(5)	.6577(2)	.3241(4)	13(1)	28(2)	15(1)	2(1)	3(1)	6(1)
C1	.5554(6)	.6227(3)	.2821(6)	21(2)	26(2)	22(2)	-2(2)	9(2)	0(2)
C2	.3831(6)	.6767(3)	.2618(6)	20(2)	32(2)	26(2)	0(2)	9(2)	-1(2)
C3	.4108(7)	.7629(3)	.2785(6)	37(2)	32(3)	28(2)	9(2)	14(2)	1(2)
C4	.6212(7)	.7964(3)	.3255(6)	39(2)	29(2)	26(2)	-5(2)	12(2)	-3(2)
C5	.7874(6)	.7429(3)	.3427(6)	20(2)	26(2)	25(2)	-4(2)	6(2)	2(2)
C6	.5180(6)	.5277(2)	.2584(6)	15(2)	28(2)	19(2)	0(1)	8(1)	1(1)

Table 15.  $\text{Cu}(\text{N-picC})_2(\text{H}_2\text{O})_2$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	.0000	.0000	.0000	35.30(4)	28.08(3)	18.47(3)	-24.09(3)	-2.34(3)	1.87(2)
O1	-.11135(5)	.20219(5)	-.21436(4)	34.5(2)	36.8(2)	25.1(1)	-24.1(1)	-3.9(1)	6.3(1)
O2	.20304(6)	.10617(5)	.05112(3)	47.8(2)	39.4(2)	17.7(1)	-33.8(2)	-2.0(1)	1.1(1)
O3	.30192(6)	.35767(5)	-.00766(4)	51.6(2)	37.4(2)	33.4(2)	-34.2(2)	-2.2(1)	-4.5(1)
O4	.28714(6)	-.25767(5)	-.16340(4)	40.9(2)	35.6(2)	40.8(2)	-24.0(2)	-1.3(2)	-1.2(1)
N1	-.04880(6)	.78083(5)	.30683(4)	33.0(2)	19.2(1)	20.9(1)	-14.4(1)	-1.1(1)	.6(1)
C1	.21757(7)	.24269(6)	-.23912(5)	30.0(2)	20.9(2)	21.8(2)	-14.2(2)	1.4(1)	-.8(1)
C2	.62610(8)	.73226(7)	.34171(5)	33.0(2)	32.3(2)	29.4(2)	-16.7(2)	5.3(2)	-.5(1)
C3	.35644(9)	.26986(8)	-.51541(6)	42.6(3)	38.9(2)	29.5(2)	-13.9(2)	13.5(2)	-3.2(2)
C4	.18179(10)	.24704(7)	-.57980(5)	54.2(3)	35.5(2)	21.5(2)	-15.0(2)	5.2(2)	-7.0(2)
C5	.97055(9)	.77794(7)	.47536(5)	46.8(3)	26.0(2)	22.6(2)	-15.9(2)	-5.8(2)	-2.4(1)
C6	.76148(7)	.76182(6)	.05098(5)	29.3(2)	29.3(2)	22.0(2)	-17.7(2)	1.7(1)	-2.7(1)

Table 16.  $M(\text{N-picO})_2(\text{H}_2\text{O})_2$ ,  $M = \text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ .

Final positional parameters and isotropic thermal parameters ( $\times 10^2$ ) for hydrogen atoms with their standard deviations.

Atom	X	Y	Z	U
$\text{Mn}(\text{N-picO})_2(\text{H}_2\text{O})_2$				
H1	.264(2)	.798(1)	.275(2)	5.3(4)
H2	.225(2)	.649(1)	.347(1)	3.2(3)
H3	.374(2)	.359(1)	.134(2)	8.9(5)
H4	.908(2)	.764(1)	.343(2)	5.0(3)
H5	.928(2)	.941(1)	.284(2)	7.1(4)
H6	.874(2)	.448(1)	.109(2)	4.8(3)
$\text{Co}(\text{N-picO})_2(\text{H}_2\text{O})_2$				
H1	.245(2)	.647(1)	.233(2)	5.1(3)
H2	.296(2)	.805(1)	.264(2)	5.2(4)
H3	.357(2)	.363(1)	.153(2)	4.4(3)
H4	.937(2)	.762(1)	.377(2)	4.4(3)
H5	.896(2)	.440(1)	.129(2)	7.6(4)
H6	.898(2)	.955(1)	.295(2)	8.1(5)
$\text{Ni}(\text{N-picO})_2(\text{H}_2\text{O})_2$				
H1	.262(8)	.648(3)	.329(7)	4(1)
H2	.324(7)	.801(3)	.256(6)	2(1)
H3	.358(8)	.366(3)	.163(7)	5(1)
H4	.931(10)	.762(4)	.373(8)	7(2)
H5	.880(10)	.968(4)	.305(8)	7(2)
H6	.876(8)	.455(3)	.120(7)	3(1)
$\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2$				
H1	.501(1)	.729(1)	.293(1)	2.5(1)
H2	.486(1)	.266(1)	.413(1)	4.4(2)
H3	.174(1)	.233(1)	.312(1)	5.8(2)
H4	.888(1)	.215(1)	.489(1)	3.5(1)
H5	.599(1)	.274(1)	.135(1)	4.6(2)
H6	.740(1)	.333(1)	.142(1)	5.7(2)

Table 17.  $\text{Mn}(\text{N-inicO})_2(\text{H}_2\text{O})_4$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms and isotropic thermal parameters ( $\times 10^2$ ) for hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Mn	.5000	.6402(2)	.7500	17.6(3)	38.7(5)	21.7(4)	0.0	2.1(3)	0.0
O1	.0717(2)	.6478(5)	.6021(2)	25(1)	52(2)	37(2)	1(2)	-1(1)	0(2)
O2	.3946(2)	.6306(6)	.7775(3)	26(2)	76(3)	60(2)	0(2)	11(1)	-3(2)
O3	-.1427(2)	.1171(7)	-.0522(3)	30(2)	103(3)	39(2)	2(2)	-6(1)	7(2)
O4	.5284(2)	.1181(5)	.3691(2)	38(2)	47(2)	32(2)	-8(2)	-2(2)	2(2)
O5	.5296(2)	.5763(5)	.3825(3)	31(2)	62(3)	38(2)	4(2)	-5(1)	-13(2)
C1	.1498(2)	.6563(8)	.7758(3)	23(2)	48(3)	30(2)	-1(2)	5(2)	4(2)
C2	.2182(2)	.6485(7)	.8339(3)	28(2)	43(2)	26(2)	1(2)	3(1)	1(2)
C3	.2733(2)	.6294(7)	.7756(3)	20(2)	27(2)	32(2)	3(2)	3(1)	3(2)
C4	.3486(2)	.6244(7)	.8406(4)	22(2)	35(3)	42(2)	-0(2)	2(2)	2(2)
C5	.2585(2)	.6168(7)	.6553(3)	34(2)	37(3)	30(2)	5(2)	10(2)	2(2)
C6	.1899(2)	.6229(8)	.5986(3)	38(2)	51(3)	22(2)	3(2)	4(2)	-6(2)
N1	.1373(2)	.3577(6)	.1584(3)	24(1)	34(2)	28(2)	-0(2)	-3(1)	-2(2)
				U					
H1	.607(2)	.827(6)	.317(3)	3(1)					
H2	.280(2)	.837(7)	.083(4)	4(1)					
H3	.799(3)	.896(8)	.115(4)	5(2)					
H4	.322(2)	.881(7)	.481(4)	4(1)					
H5	.041(3)	.660(9)	.441(5)	7(2)					
H6	.514(4)	.038(11)	.123(6)	12(3)					
H7	.503(3)	.637(8)	.112(4)	5(2)					
H8	.066(4)	.085(11)	.432(6)	13(3)					



Table 18.  $\text{Fe}(\text{N-ino})_2(\text{H}_2\text{O})_6$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Fe	1.0000	1.0000	1.0000	37.8(3)	28.6(3)	16.3(2)	14(1)	-3.3(2)	5(2)
O1	1.4561(3)	.9694(11)	.8317(2)	47(1)	169(10)	20(1)	-9(3)	-12(1)	-2(2)
O2	1.1410(4)	1.1085(3)	.3348(2)	66(2)	39(2)	34(1)	14(1)	-15(1)	1(1)
O3	1.1862(3)	.8852(3)	.3260(2)	52(2)	44(2)	29(1)	-1(1)	-7(1)	-4(1)
O4	.9872(3)	1.1535(3)	.8763(2)	40(1)	39(1)	22(1)	3(1)	-3(1)	2(1)
O5	.9572(3)	1.1367(3)	1.1372(2)	35(1)	43(2)	27(1)	-2(1)	-3(1)	-6(1)
O6	1.2699(3)	1.0277(5)	1.0172(2)	47(1)	61(4)	33(1)	0(1)	-10(1)	0(1)
N1	1.3891(4)	.9733(7)	.7243(2)	41(1)	72(6)	20(1)	-7(2)	-6(1)	1(2)
C1	1.3454(5)	1.0971(5)	.6807(3)	58(3)	61(3)	30(2)	-20(2)	-1(2)	-14(2)
C2	1.2743(5)	1.1083(4)	.5664(3)	48(2)	46(2)	33(2)	-7(2)	4(2)	-1(2)
C3	1.3085(5)	.8693(5)	.5509(3)	42(2)	63(2)	31(2)	19(2)	-5(2)	11(2)
C4	1.3667(6)	.8609(5)	.6634(3)	53(2)	74(3)	29(2)	19(2)	-7(2)	-3(2)
C5	1.2597(4)	1.0075(17)	.5011(2)	37(2)	50(3)	24(1)	16(6)	-7(1)	1(5)
C6	1.1894(4)	1.0171(9)	.3772(2)	43(1)	12(5)	25(1)	-3(2)	-7(1)	-5(2)

Table 19.  $\text{Co}(\text{N-inicO})_2(\text{H}_2\text{O})_6$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Co	1.0000	1.0000	1.0000	29.3(2)	23.9(1)	15.6(1)	1.7(3)	-5.2(1)	.5(3)
O1	1.4554(2)	.9895(4)	.8332(1)	37(9)	241(3)	22.3(7)	6(2)	-11.0(6)	1(2)
O2	1.1521(3)	1.1062(2)	.3348(1)	80(1)	41(1)	36(1)	16(1)	-23(1)	-2(1)
O3	1.1789(3)	.8822(2)	.3259(1)	70(1)	33(1)	32(1)	-7(1)	-16(1)	-3(1)
O4	.9817(3)	1.1560(1)	.8791(1)	80(1)	37(1)	30(1)	-7(1)	-22(1)	9(1)
O5	.9618(1)	1.1296(2)	1.1375(1)	67(1)	42(1)	31(1)	18(1)	-21(1)	-9(1)
O6	1.2657(2)	1.0343(2)	1.0180(1)	36(1)	94(2)	35(1)	0(1)	12(1)	-3(1)
N1	1.3890(2)	.9888(4)	.7261(1)	27(1)	136(2)	23(1)	-2(1)	-8(1)	8(2)
C1	1.3314(4)	1.1051(4)	.6810(2)	54(2)	99(3)	36(1)	-5(2)	-6(1)	-28(2)
C2	1.2651(4)	1.1102(3)	.5683(2)	48(2)	62(2)	34(1)	3(1)	-6(1)	-9(1)
C3	1.3181(3)	.8735(3)	.5517(2)	45(1)	51(2)	32(1)	-5(1)	-8(1)	14(1)
C4	1.3801(4)	.8711(4)	.6641(2)	45(2)	98(3)	38(1)	5(2)	-10(1)	19(2)
C5	1.2600(3)	.9922(3)	.5014(2)	30(1)	44(1)	24(1)	-9(2)	-8(1)	14(1)
C6	1.1900(3)	.9932(3)	.3781(1)	34(1)	37(1)	25(1)	6(2)	-8(1)	19(1)

Table 20. Ni(N-inicO)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>. Fractional atomic coordinates and anisotropic thermal parameters

( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Ni	1.0000	1.0000	1.0000	28.8(3)	20.0(2)	15.5(2)	.9(4)	4.2(2)	.0(4)
O1	1.4563(3)	.9793(5)	.8363(2)	41(2)	168(4)	21(1)	14(2)	-11(1)	-2(2)
O2	1.1489(4)	1.1060(3)	.3347(2)	72(2)	35(1)	32(1)	11(1)	-18(1)	2(1)
O3	1.1853(4)	.8791(2)	.3227(2)	69(2)	28(1)	29(1)	-4(1)	-14(1)	-1(1)
O4	.9638(4)	1.1613(2)	.8887(2)	59(2)	34(1)	29(1)	-4(1)	-14(1)	6(1)
O5	.9690(4)	1.1205(3)	1.1413(2)	55(2)	37(1)	26(1)	15(1)	-13(1)	-8(1)
O6	1.2583(3)	1.0477(3)	1.0162(2)	35(1)	57(2)	30(1)	-2(1)	-12(1)	-1(1)
N1	1.3904(4)	.9814(5)	.7284(2)	35(2)	95(3)	20(1)	-1(2)	-9(1)	-1(2)
C1	1.3183(6)	1.0993(5)	.6865(3)	47(2)	67(3)	37(2)	-1(2)	2(2)	-19(2)
C2	1.2539(5)	1.1037(4)	.5726(3)	47(2)	45(2)	27(2)	2(2)	-7(2)	-7(2)
C3	1.3329(5)	.8688(4)	.5474(3)	37(2)	44(2)	35(2)	-2(2)	-3(2)	8(2)
C4	1.3969(5)	.8682(5)	.6611(3)	39(2)	77(2)	34(2)	6(2)	-9(2)	19(2)
C5	1.2610(4)	.9868(4)	.5017(2)	30(1)	32(2)	23(1)	-8(1)	-6(1)	2(2)
C6	1.1920(5)	.9908(5)	.3766(2)	38(2)	35(2)	35(2)	23(1)	-10(1)	4(2)

Table 21.  $M(\text{N-inicO})_2(\text{H}_2\text{O})_6$ ,  $M = \text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ .

Final atomic coordinates and isotropic thermal parameters ( $\times 10^2$ ) for hydrogen atoms with their standard deviations.

	X	Y	Z	U
$\text{Fe}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
H1	.663(5)	.814(5)	.264(4)	8(1)
H2	.170(8)	.303(7)	.048(6)	16(2)
H3	.308(6)	.703(5)	.017(4)	9(2)
H4	.556(9)	.218(7)	.300(6)	17(3)
H5	.289(7)	.977(10)	.009(5)	22(3)
H6	.348(7)	.033(20)	.073(5)	17(2)
H7	.113(7)	.380(6)	.378(5)	14(2)
H8	.055(8)	.849(7)	.194(6)	19(3)
H9	.044(6)	.133(5)	.191(4)	7(1)
H10	.055(4)	.720(4)	.378(3)	2(1)
$\text{Co}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
H1	.663(3)	.811(3)	.273(2)	5(1)
H2	.219(4)	.306(3)	.037(3)	10(1)
H3	.315(4)	.718(3)	.017(2)	9(1)
H4	.557(4)	.223(4)	.306(3)	9(1)
H5	.274(4)	.945(3)	.017(2)	11(1)
H6	.334(4)	.029(4)	.086(3)	13(1)
H7	.074(4)	.375(3)	.378(3)	11(1)
H8	.070(5)	.858(4)	.199(3)	13(1)
H9	.054(4)	.126(3)	.193(2)	9(1)
H10	.068(3)	.713(2)	.380(2)	3(1)
$\text{Ni}(\text{N-inicO})_2(\text{H}_2\text{O})_6$				
H1	.686(6)	.824(4)	.261(3)	6(1)
H2	.205(4)	.319(4)	.039(4)	7(1)
H3	.342(7)	.722(5)	.001(4)	8(2)
H4	.543(7)	.202(5)	.305(4)	8(2)
H5	.852(7)	.985(7)	.013(7)	12(2)
H6	.314(5)	.028(4)	.056(3)	6(1)
H7	.072(7)	.351(6)	.370(4)	12(2)
H8	.079(8)	.854(6)	.168(5)	13(2)
H9	.039(6)	.109(5)	.198(4)	9(2)
H10	.092(7)	.695(5)	.366(4)	11(2)

Table 22.  $\text{Cu}_4(\text{N-inicO})_4\text{SO}_4(\text{OH})_2(\text{H}_2\text{O})_4$ . Fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^3$ ) for non-hydrogen atoms with their standard deviations.

	X	Y	Z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu1	.0750(2)	.2226(	.0036(2)	19.0(9)	30(1)	18.8(8)	1(1)	14.2(7)	0(1)
Cu2	.1813(2)	.2998(5)	1.2420(2)	15.3(9)	24(1)	18.2(8)	-3(1)	13.3(7)	-3(1)
S1	.0000	-.3409(11)	1.0000	29(4)	14(3)	40(4)	0	13(3)	0
O1	.0798(10)	.1589(23)	.1057(9)	21(6)	45(9)	21(6)	5(6)	17(5)	0(6)
O2	.9286(10)	.2088(36)	.0975(10)	26(7)	106(15)	22(6)	-18(10)	19(6)	-11(9)
O3	.0920(10)	.3084(30)	.2539(10)	23(6)	51(10)	30(6)	-13(8)	22(5)	-13(8)
O4	.8687(11)	.2798(27)	.3643(10)	35(7)	32(9)	38(7)	-10(7)	32(6)	-8(7)
O5	.2278(10)	.2125(34)	.1094(10)	19(6)	92(13)	23(6)	8(9)	14(5)	-6(9)
O6	.2974(9)	.3072(29)	.2650(10)	22(6)	49(9)	29(6)	-6(8)	23(5)	-7(8)
O7	.2050(9)	.7711(26)	.3992(10)	20(6)	37(11)	33(6)	-2(7)	19(5)	-9(7)
O8	.5691(17)	.0105(59)	.0089(20)	36(11)	284(40)	90(15)	-19(20)	54(12)	20(23)
O9	.5661(15)	.2925(40)	.0954(12)	76(12)	57(13)	34(8)	2(14)	24(8)	4(11)
O10	.2677(11)	.0602(24)	.3577(10)	38(8)	32(8)	30(6)	11(7)	26(6)	8(6)
O11	.2663(11)	.5100(22)	.3535(11)	33(8)	24(8)	36(7)	-3(6)	28(6)	-3(6)
N1	.3973(12)	.7757(30)	.3227(11)	32(8)	31(11)	29(7)	2(8)	27(7)	2(8)
N2	.1093(11)	.7709(24)	.3535(11)	18(6)	14(10)	27(6)	-2(6)	18(6)	-5(6)
C1	.8239(15)	.2542(37)	.2140(14)	35(10)	26(16)	23(8)	2(10)	21(8)	1(8)
C2	.3551(15)	.7479(40)	.1723(14)	28(9)	39(16)	27(8)	4(10)	21(8)	3(9)
C3	.9631(13)	.2667(34)	.2382(12)	17(7)	34(17)	16(6)	-2(8)	14(6)	-1(8)
C4	.0380(14)	.2819(36)	.3518(12)	26(8)	21(11)	24(7)	-6(9)	20(7)	-0(8)
C5	.5035(14)	.7869(37)	.3905(12)	27(9)	20(9)	23(7)	-1(10)	19(7)	-0(9)
C6	.4985(15)	.7644(41)	.1950(14)	33(10)	41(20)	26(8)	1(11)	25(8)	-1(10)
C7	.6036(13)	.2837(35)	.4170(11)	22(8)	25(10)	17(6)	-9(9)	15(6)	-2(8)
C8	.5047(13)	.2846(36)	.3723(13)	15(7)	23(10)	24(7)	1(9)	14(6)	-6(9)
C9	.4112(13)	.2707(37)	.2579(12)	12(7)	38(17)	19(6)	2(9)	9(6)	2(8)
C10	.9208(14)	.7564(41)	.1966(14)	23(9)	46(20)	27(8)	4(10)	19(7)	0(10)
C11	.5204(14)	.2577(42)	.2424(14)	23(9)	42(20)	25(8)	2(10)	16(7)	-3(10)
C12	.8019(14)	.7645(46)	.2074(14)	18(8)	55(22)	24(8)	-9(11)	12(7)	-10(11)