

Synthesis, crystal structure and selected properties of two new peroxidomolybdates

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ABSTRACT

Two new oxidoperoxidocompounds with isonicotinic acid *N*-oxide have been obtained and characterized. Both compounds are oxidodiperoxidomolybdates built with the same isonicotinic acid *N*-oxide moiety, first one – potassium salt: $K(C_6H_4MoNO_8)H_2O$ (denoted as **K-isoO**) and the ammonium salt: $(NH_4)_2(C_6H_4MoNO_8)_2 \cdot 2H_2O$ (**NH₄-isoO**). They were investigated using powder X-ray diffraction (**K-isoO**) or single crystal (**NH₄-isoO**) techniques. In addition, they were examined with the use of XRPD versus temperature method, IR spectroscopy and catalytic activity studies. This work is also a continuation of our previous papers and presents a summary of studies of peroxidomolybdates forming inorganic–organic hybrids with pyridine carboxylic acids.

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1. Introduction

Peroxidocompounds are a subgroup of polyoxocompounds (POMs). POMs are described as clusters of transition metal ions surrounded by oxygen atoms. Candidates for metal precursors (atoms creating POMs) used should be on the highest degree of oxidation. Metals used the most frequently are tungsten, vanadium, niobium, tantalum, and molybdenum [1,2]. One way of obtaining peroxocompounds is the reaction of hydrogen peroxide with transition metal precursors [3]. A detailed classification of peroxocompounds was presented by Harald et al. 2007 [4].

There exist many scientific reports on the properties of POMs. They are well known as catalysts, reagents in green chemistry processes and ingredients of medicines. It has been proven that they possess catalytic properties on olefin epoxidation [5] and oxidation of cyclooctane [6,7]. Interesting biological activity has been found for Keggin-type polyoxometalates containing glycine, where the compound acts as mushroom tyrosinase inhibitors [8]. Moreover, special attention should be given to antitumor capacity, for example $[(C_{16}H_{33})_2NCONH(CH_2)_3SiNaP_5W_{29}O_{110}]^{14-}$ hybrid (polyoxometalate-based organic–inorganic hybrids) have antitumor

activity in terms of cancer cell lines HT29 [9]. In addition, Bijelic et al. [10] published a review article in 2018, where they presented a wide range of different POMs, their antitumor capacity and also proposed mechanisms of the anticancer activity of polyoxometalates. In 2017, Wang et al. [11] presented a spectacular article where they claim that pyridinium polyoxometalates work as inhibitors against HIV-1 virus and also have a lower toxicity to T2M-bl cells than other currently used methods.

Peroxocompounds are much less known and studied. They possess specific character associated with the properties of one of the substrates, which is hydrogen peroxide. This results in embedding in the structure precursors of reactive forms of oxygen, with the possibility of generating dioxygen in its first excited singlet state (1O_2), which induces unique properties of materials based on peroxocompounds.

Peroxomolybdates and peroxovanadates have found a wide application in green chemistry as catalysts. Conte and Floris [3] presented a review article about catalytic properties, where they classified peroxocompounds regarding the type of oxidation: oxidation of substrates containing sulphur and nitrogen, oxidation of alcohols, oxidation of alkenes. Similar properties were claimed by Dzierbiński et al. [12], where peroxocompounds with Mo, V, W have been used in epoxidation of allyl-alcohol with hydrogen peroxide. In addition, peroxomolybdates have been used in the bleaching process [13]. On the other hand, Nasrin et al. [14] examined peroxomolybdates for metallurgic properties and biological

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activity. Our group also studied catalytic activity and potential of peroxocompounds [7,15–17].

First examinations of oxidodiperoxocompounds with pyridine-carboxylic acid were presented in 1988 when Djordjevic et al. [18] obtained six peroxocompounds based on vanadium(V) and molybdenum(VI) with nicotinic acid and nicotinic acid *N*-oxide. Our group has conducted similar research for several years now [16]. In particular, we obtained pure phases described by Djordjevic [18], in the form of single crystals, and we determined their crystal structures [16]. The subsequent goal was to obtain new peroxomolybdates with different derivatives of pyridine-carboxylic *N*-oxide acid. Based on our previous work [16,17], we expected that many different peroxidomolybdates can result from the use of various derivatives of pyridine-carboxylic acid.

The main idea of this work is explained in Fig. 1. Starting from an alkaline solution, after relatively mild and quick acidification, we can expect a low degree of polycondensation – the predominance of mono-nuclear or low-nuclear forms – of peroxidomolybdates. By adding different pyridine-carboxylic acid isomers, we can expect different forms of inorganic-organic peroxidomolybdates due to the different distances of the potential chelating groups: N (or N → O) and –COO[−]. In our previous studies we tested compounds with picolinic (2-carboxy) or nicotinic (3-carboxy) acid *N*-oxides (abbreviated as **pico** and **nic**) [16,17], obtaining simple mono-, or cyclic dimeric structures. In the present work we have tested complexes with isonicotinic acid *N*-oxide (4-carboxy; **iso**), expecting more complex dimeric or even polymeric structures.

The purpose of this study is to present two new peroxide-Mo compounds obtained with isonicotinic acid *N*-oxide, their crystal structure and physicochemical properties based on IR spectroscopy, thermal decomposition, and their catalytic properties in the reaction of oxidation of cyclooctane. Moreover, this paper will report some general remarks on work already carried out in this area by our group [16,17].

2. Experimental

2.1. Materials

Inorganic chemicals containing molybdenum (K₂MoO₄, (NH₄)₆-Mo₇O₂₄·4H₂O – HMA), HCl (conc.), KCl and NH₃aq(conc.) were

Table 1
Summary of crystal data of the investigated compounds.

Compound code, (XRD technique)	K-isoO (polycrystals)	NH ₄ -isoO (single crystals)
Chemical formula	C ₆ H ₄ K ₁ Mo ₁ N ₁ O ₉	C ₆ H ₁₀ Mo ₁ N ₂ O ₉
Chemical formula, structural*	K(C ₆ H ₄ MoNO ₈)H ₂ O	(NH ₄) ₂ (C ₆ H ₄ MoNO ₈) ₂ 2H ₂ O
MW (g/mol)	369.1	350.10
T(K)	293	293(2)
Wavelength, [Å]	CuKα: 1.54184	CuKα: 1.54184
Crystal system	Monoclinic, P 1 2 ₁ /n 1	triclinic, P – 1
Cell parameters:		
a[Å]	9.2477(3)	6.5619(3)
b[Å]	19.5475(5)	7.1063(3)
c[Å]	6.9631(2)	12.0469(4)
α[°]	90	91.517(3)
β[°]	111.311(3)	96.093(3)
γ[°]	90	104.610(4)
V(Å ³)	1172.65(7)	539.69(4)
Z, calculated density (g/cm ³)	4, 2.0909	1, 2.154
absorption coefficient (mm ^{−1})	12.775	10.461
F(0 0 0)	720	348
theta range	3.014–74.992	3.70–76.98
limiting indices	−7 ≤ h ≤ 6; 0 ≤ k ≤ 15; 0 ≤ l ≤ 5	−7 ≤ h ≤ 8; −8 ≤ k ≤ 8; −15 ≤ l ≤ 15
reflections collected/unique	610	2241/2205
completeness to theta	100% (powder sample)	76.98, 98,2%
absorption correction	Capillary, calc. for cylindrical sample	Multiscan
maximum and minimum transmission	n.a. (powder sample)	1.000; 0.2947
refinement method	Rietveld	F2 (Fsqd)
data/restraints/parameters	5483/38/78	2241/0/191
goodness of fit on F2	3.59	0.973
Final R indices [I > 2σ (I)]	R _p = 4.57, R _w p = 1.59	R1 = 3.60, wR2 = 10.30
R indices (all data)	R _f = 6.44	R1 = 3.55, wR2 = 10.23
extinction coefficient	–	None
Largest difference peak and hole (eÅ ^{−3})	–	−1.598; 1.134
CCDC	1943663	1943662

*Idealized formula, in **K-isoO** hydrogen atoms in H₂O were not located.

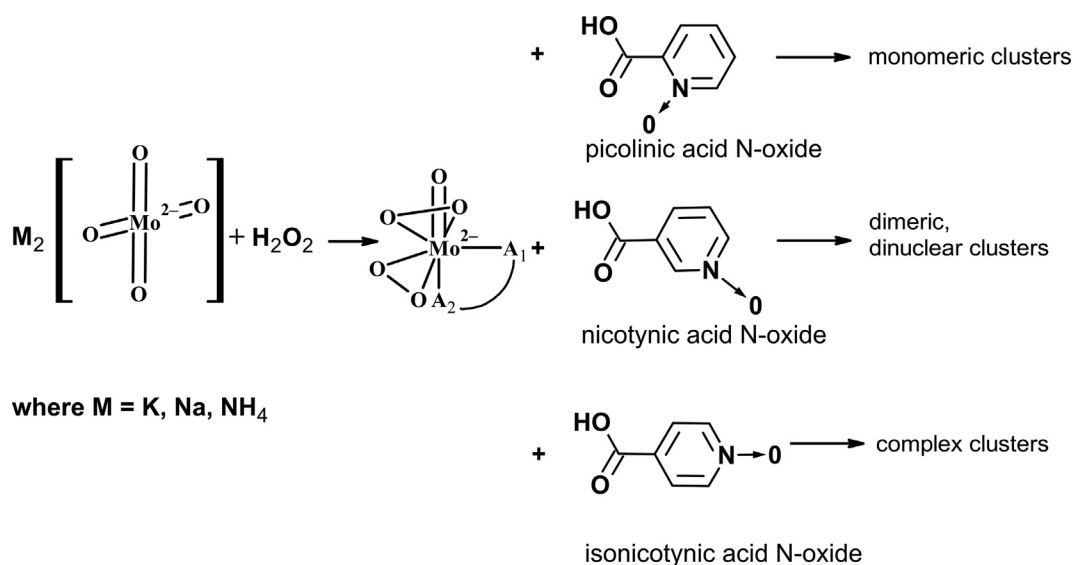


Fig. 1. The proposed reaction types of oxidodiperoxido-Mo (VI) centers with various pyridine-carboxylic acids *N*-oxides.

purchased from Avantor (formerly POCh Gliwice). Isonicotinic acid *N*-oxide and H₂O₂ (30%) were purchased from Sigma–Aldrich Corporation.

2.2. Syntheses

Both compounds were obtained directly during the reaction from water solutions. The first one

K-isoO was obtained immediately (during reaction), while the second one (**NH₄-isoO**) after ~1 week. Both compounds were synthesized in good yield. Both syntheses were conducted in similar manner as previously described syntheses of similar compounds with nicotinic and picolinic acids [16,17].

Table 2
Selected bond lengths (Å) in the studied compounds.

K-isoO		NH ₄ -isoO	
atom1-atom2	value [Å]	atom1-atom2	value [Å]
Mo–O2	1.629(9)	Mo–O7	1.680(3)
Mo–O3	1.951(15)	Mo–O2	1.924(3)
Mo–O4	2.027(15)	Mo–O5	1.940(3)
Mo–O5	1.918(14)	Mo–O1	1.943(3)
Mo–O6	2.069(13)	Mo–O6	1.945(3)
Mo–O7	2.111(16)	Mo–O3	2.059(3)
Mo–O16	2.51(1)	Mo–O8 ⁱ	2.431(3)
O3–O4	1.36(2)	O2–O1	1.478(4)
O5–O6	1.36(2)	O5–O6	1.479(4)
O7–C8	1.39(2)	O4–C1	1.210(5)
C8–O9	1.412(19)	O3–C1	1.313(5)
N13–O16	1.426(18)	N6–O8	1.333(4)

Potassium [poly-bis(η²-peroxido)oxido-μ-(1-oxo-κO-pyridine-4-carboxylate-κO)]molybdate(VI) hydrate, (**K-isoO**).

0.02 mol KCl and 0.005 mol K₂MoO₄·H₂O were dissolved in 20 ml of cold H₂O₂. The resulting red solution was acidified by drops of concentrated HCl until it changed color to yellow. Next 0.005 mol of *N*-oxide isonicotinic acid was added to the yellow solution which was left for one hour with stirring. Obtained large amount of yellow solid. Yield 94% (1.65 g) C 21.47 (cal. 19.42) H 1.667 (cal. 1.66) N 4.18 (cal. 3.77).

Diammonium [tetrakis(η²-peroxido)dioxido-bis{μ-(1-oxo-κO-pyridine-4-carboxylate-κO)}dimolybdate(VI) dihydrate, (**NH₄-isoO**).

1.43 mmol HMA was dissolved in 20 ml of cold H₂O₂. To the resulting transparent solution 1 ml of NH₃aq was added. Next, the obtained red solution was acidified by drops of HCl until it changed color to yellow. Subsequent step was the addition of 0.005 mol of *N*-oxide isonicotinic acid to the solution. Prepared yellow, transparent solution was left for one hour with stirring. The solution was left to crystallize. Yellow crystals were obtained after 1 week. Yield 87% C 20.42 (cal. 20.58) H 2.844 (cal. 2.88) N 8.22 (cal. 8.00).

2.3. X-ray powder/single crystal diffraction data analysis

The X-ray powder diffraction (XRPD) investigations were performed for **K-isoO** and single crystal X-ray diffraction (XRD) for **NH₄-isoO**. The temperature during measurements was 293(2) K. X-ray powder diffraction data were collected using PANalytical X'Pert Pro MPD diffractometer, and single-crystal data using a SuperNova (Oxford Diffraction). High Score software and the

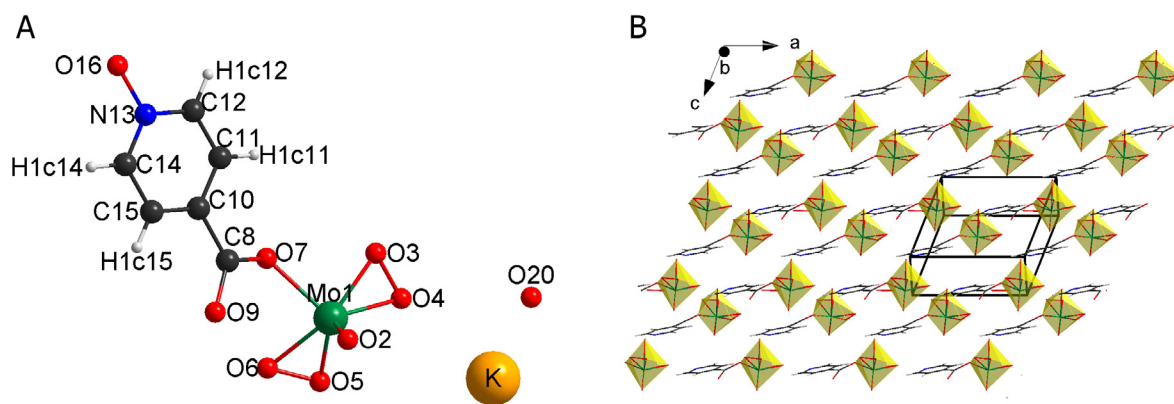


Fig. 2. (A) The asymmetric unit of **K-isoO**; (B) packing diagram of **K-isoO**.

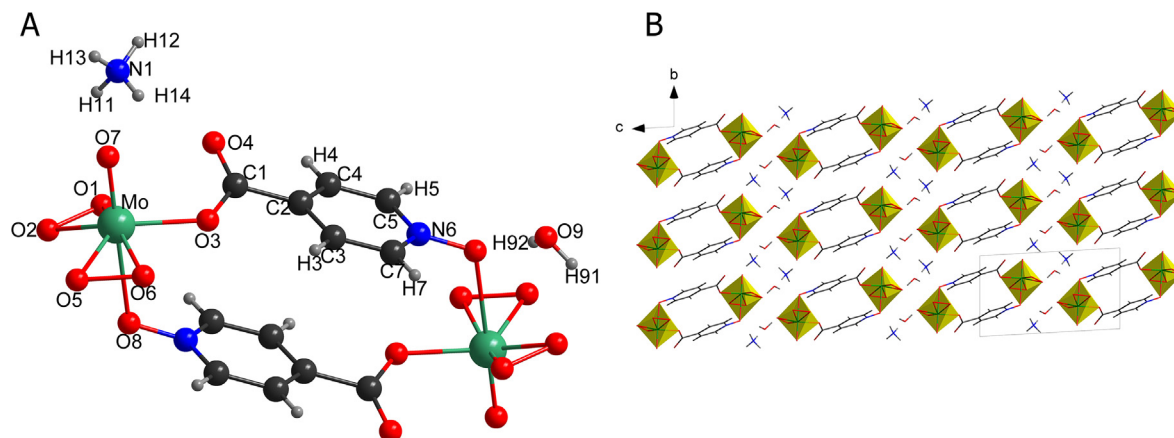


Fig. 3. (A) The asymmetric unit of **NH₄-isoO**; (B) packing diagram of **NH₄-isoO**.

Table 3
IR spectra vibrations and band assignments connected with oxodiperomolybdate [15,26] and nicotinic acid *N*-oxide, picolinic acid *N*-oxide moiety for compounds [27]. Vs-very strong, s-strong, m-medium, w-weak.

Compound	$\nu(\text{M}=\text{O})$	$\nu_{\text{sym}}(\text{O}-\text{O})$	$\nu_{\text{sym}}(\text{M}-(\text{O})_2)$	$\nu_{\text{asym}}(\text{M}-(\text{O})_2)$	(<i>N</i> -oxide) vibrations
1 K-isoO	968.03 s, 959.37vs	883.61 s, 867.06vs	544.27 m	588.72 s,	814.94 m, 484.63w
2 NH₄-isoO	964.66vs	869.30vs, 861.43vs, 837.32w	554.97w, 543.16 m, 525.54w	585.17 s	808.91 m, 485.88w

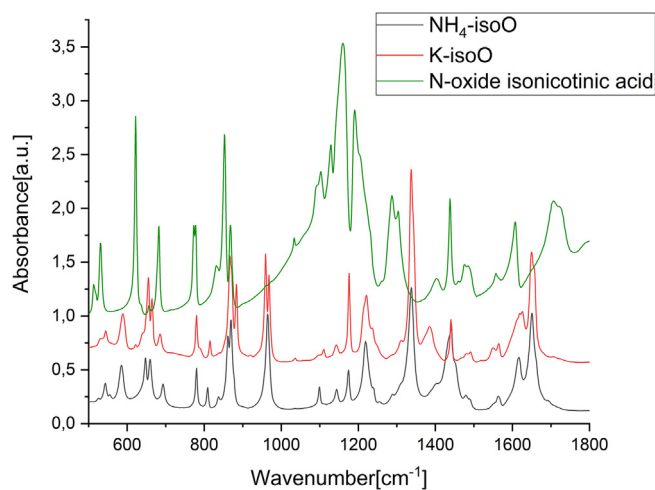


Fig. 4. IR spectra of the compounds **NH₄-isoO**, **K-isoO**, and isonicotinic acid *N*-oxide.

PDF-4+ [ICDD, 2018] database were used for initial analysis of powder diffraction data.

Structure solution and refinement of **NH₄-isoO** were performed using SHELXS-97 and SHELXL-2013 programs [19]. To find location of hydrogen atoms difference Fourier maps were used. For all non-hydrogen atoms anisotropic refinement was used. Powder diffraction studies were performed using Expo2014 program [20] to locate Mo and K atoms, and FOX [21] to find position and orientation of isonicotinic acid moiety. Finally restrained Rietveld refinement was performed with the use of Jana2006 [22]. Detailed crystal structure data for **K-isoO** and **NH₄-isoO** are presented in Table 1.

The Diamond [23] and Mercury [24] programs were used for visualization of the crystal structures of the obtained compounds.

2.4. IR measurements

The infrared spectra (IR) were measured on a Bruker VERTEX 70V. Samples were triturated and pressed into the pellets with KBr (1 mg sample for 100 mg KBr). The samples were analyzed

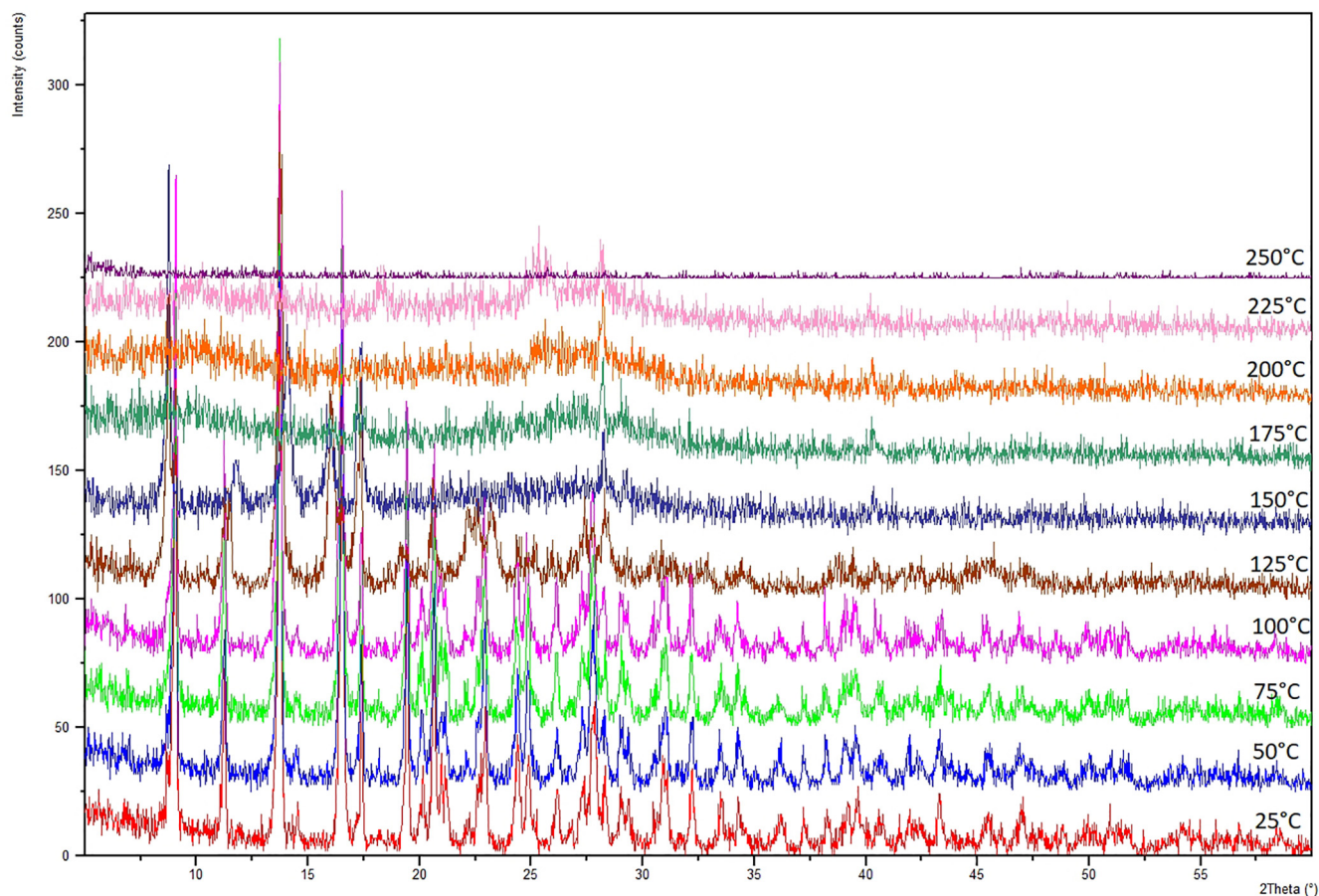


Fig. 5. Thermal decomposition for the compound **K-isoO** (see text for description).

at room temperature. The Origin Pro v. 9.1 [25] was used for analysis of IR spectra.

2.5. X-ray thermal decomposition

X-ray thermal decomposition patterns were measured using Philips X'Pert Pro MPD. X-ray data for **K-isoO** compounds was collected at the following temperatures: 25, 50, 75, 100, 125, 150, 175, 200, 225, 250 °C, while for **NH₄-isoO** the measurements were done at 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 300, 350, 400, 450, 500, 550, 600 °C and again 25 °C. The 2θ range was from 5 to 70°. The heating rate was 5 °C/min, the cooling rate was 10 °C/min.

2.6. Catalytic activity

In this study the oxidation of cyclooctane was performed as previously described [7,16,17]. The experiment was carried out in a stainless steel batch reactor system at 120 °C and under an air pressure of 10 atm. The cyclooctane-to-oxygen molar ratio was set at 6.5. Cooling of the hot reactor took place after 6 h and it stopped the oxidation. The oxidation products cyclooctanone and cyclooctanol were analyzed by an Agilent 6890 N Gas Chromatograph equipped with an Innowax (30 m) column in the presence of an internal standard (chlorobenzene).

3. Results and discussion

3.1. Crystal structure data

Detailed crystal data are shown in Table 1. Table 2 presents a list of chosen bond distances, Table SI-1 (Supplementary Material) pre-

sents selected angles in the investigated compounds. Rietveld refinement plots for **K-isoO** is presented also in SI (Fig. SI-1). **K-isoO** structure is presented in Fig. 2 A-B, while **NH₄-isoO** is shown in Fig. 3A-B. Both compounds contain the same isonicotinic acid *N*-oxide building block. Also, both compounds are hydrated potassium and ammonium salts. The essential feature of the first compound is polymeric anion, whereas the second compound is formed by centrosymmetric cyclic anions. In both obtained compounds two oxygen atoms join the organic part with the inorganic part. The linking oxygen atoms belong to *N*-oxide group and to carboxylic group (see Fig. 2A and Fig. 3A). In both compounds, pentagonal bipyramids MoO₇ are present. This means that each Mo atom is surrounded by seven oxygen atoms. Moreover, two peroxy groups are observed in the equatorial plane of the pentagonal bipyramid. One apical terminal oxygen atom is observed in each compound (M=O distance in **K-isoO**: 1.63(1) Å; in **NH₄-isoO**: 1.680(3) Å). The Mo atom is moved from the equatorial plane of the pentagonal bipyramid by 0.655(3) Å for **K-iso** and by 0.4228(2) Å for **NH₄-iso**. The equatorial plane is twisted with respect to the pyridine ring by 23.9(7)° and 18.38(3)° in compounds **K-isoO** and **NH₄-isoO**.

The organic parts are represented by *N*-oxide-pyridine rings for both cases. π - π interactions are observed for the pyridine fragments. The shortest distance between the atoms of neighboring aromatic rings is 3.89(1) Å for **K-isoO** and 3.269(5) Å for **NH₄-isoO**. Respectively, distances between centroids of relevant rings are 4.73 and 3.954 Å.

3.2. IR spectra

The observed IR spectra of both compounds are very similar, especially in the range of <1000 cm⁻¹, which indicates the same

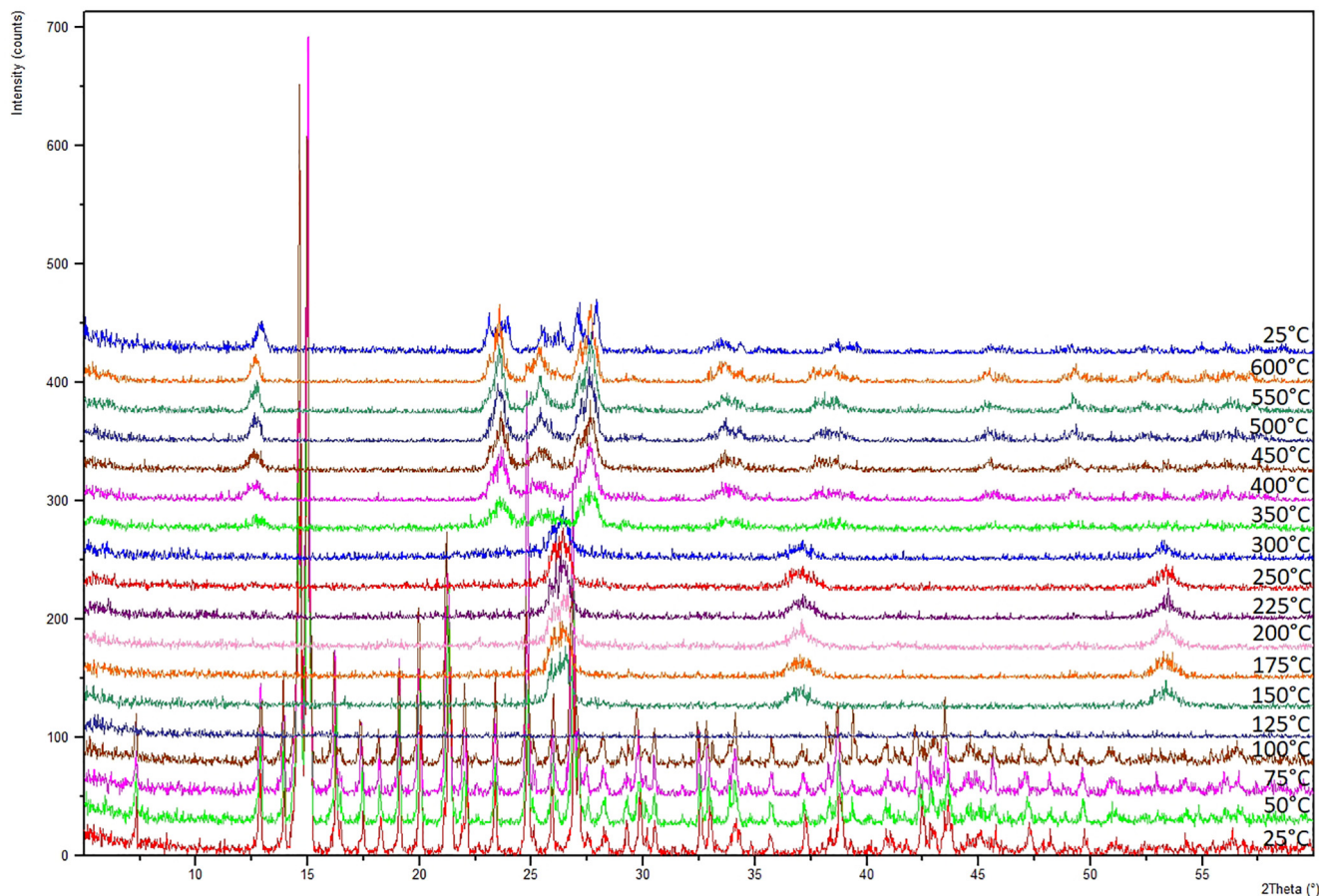


Fig. 6. Thermal decomposition for the compound **NH₄-isoO** (see text for description).

structure of the oxidodiperoxido-Mo group Table 3. Some differences, as one can expect, are in the range characteristic for H-bonds. For the sake of comparison, Fig. 4 contains also IR spectrum of isonicotinic acid *N*-oxide. Detailed inspection indicates that final products do not contain *N*-oxide admixtures, though some vibrations are preserved, indicating incorporation of *N*-oxide moiety into hybrid molecule.

3.3. Thermal decomposition

The relation between thermal stability and molecular structure was elaborated on the basis of thermal decomposition investigations. XRPD versus temperature demonstrated the stability of both compounds up to 100 °C. The **K-isoO** (polymeric structure) decomposed to new, not identified so far phase ~125 °C. Subsequently, it decomposed to amorphous phase in 250 °C (Fig. 5). After heating and cooling the sample became swollen. The **NH₄-isoO** (dimeric, without water in Mo coordination sphere) decomposed to the amorphous phase (125 °C), and then molybdenum dioxide [pdf-4

+ 00-032-0671] was formed at 150 °C–300 °C, which finally recrystallized into molybdenum trioxide (350 °C–600 °C) [PDF-4+ 04-004-5433]. This phase (MoO₃) was stable after cooling to 25 °C (Fig. 6). After heating and cooling the sample was a little swollen and a small amount of the sample was lost.

4. Catalytic activity

In the case of **K-isoO**, we observed very little catalytic activity. Analogous results were observed for compounds containing Mo (VI) centers, similar to MoO₃, with a compact structure preventing the penetration of ingredients, not wettable by organic reagents [7]. This may be correlated with the dense polymeric structure of **K-isoO**. The polymeric structure causes partial blockage of some catalytic centers, they become available only after dissolution of the polymeric material at the compound decomposition step.

NH₄-isoO exhibits relatively high catalytic activity, comparable to the nicotinic acid ammonium complex (**NH₄-nicO**, see Table 4). Both compounds have a very similar structure, their crystal

Table 4
Oxidation of cyclooctane using molybdenum complexes.

Catalyst number and code	Cyclooctanone [%]	Cyclooctanol [%]	Cyclooctanone + Cyclooctanol	Cyclooctanone/cyclooctanol
1 K-isoO	1.0	0.8	1.8	1.25
2 NH ₄ -isoO	29.7	7.3	37	4.07
Examples from previous studies [16,17]				
NH ₄ -nicO	32.9	20.2	53.1	1.6
K-nicO	5.1	4.1	9.2	1.2
NH ₄ -picO	32.0	18.4	50.4	1.7
K-picO	13.6	13.6	27.2	1.0

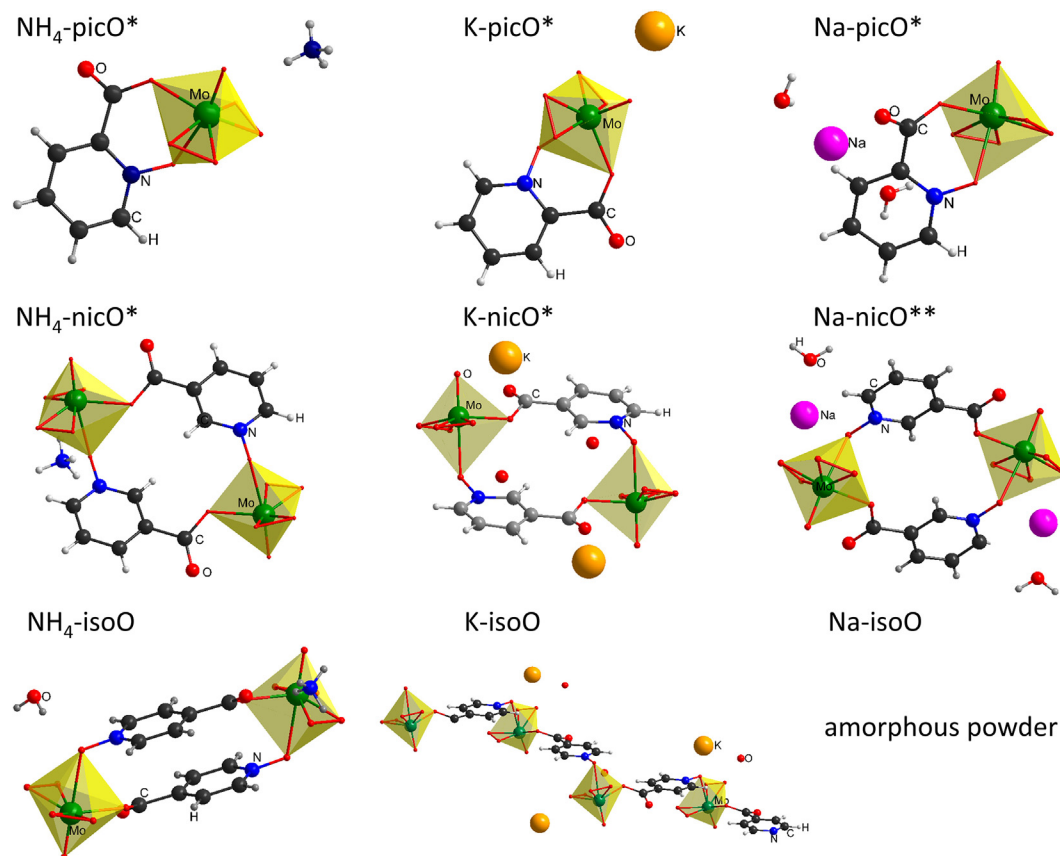


Fig. 7. Essential building blocks observed in the family of hybrid oxidodiperoxidomolybdates of pyridine carboxy acids *N*-oxides. Symbols (*) and (**) indicate results of our earlier investigations: * – [17]; ** – [16].

structures contain isolated centrosymmetric dimers and two oxidodiperoxidomolybdate groups. Very interesting is the high efficiency of the ketone form when **NH₄-isoO** was used as a catalyst.

An additional conclusion can be formulated as follows: oxidodiperoxidomolybdates of ammonium with the same (or closely related) structure as their potassium analogs are much more active in the tested reactions of catalytic oxidation of cyclooctane.

5. Conclusions

To sum up, the knowledge of the family of compounds of pyridine carboxy acids with oxidodiperoxidomolybdate groups has been extended. In particular, two new oxidodiperoxidomolybdate compounds with isonicotinic acid *N*-oxide were obtained. Their crystal structures were determined from single crystal – **NH₄-isoO**, and XRPD data – **K-isoO**. Oxidodiperoxidomolybdenum compounds containing isonicotinic acid *N*-oxide form dimeric cyclic anions – **NH₄-isoO**, or polymeric structure – **K-isoO**.

The IR spectra were recorded for both compounds and these examinations have confirmed existing peroxo bonds. The thermal stability has been tested. Both compounds are stable up to 100 °C. The catalytic activities in cyclooctane oxidation reactions were investigated, these activities have been linked to the crystal structure of investigated compounds. The oxidodiperoxidomolybdates of ammonium are more active catalysts in comparison with potassium analogs.

All oxidodiperoxidomolybdate compounds obtained by our group so far are shown in Fig. 7. It can be concluded that COO- and N → O in ortho positions lead to monomeric complexes, meta position leads to dinuclear complexes and para position leads to either dinuclear or polymeric structures.

Despite many efforts, **Na-isoO** could not be obtained in crystalline form enabling us to perform structural investigations. Further work aimed at obtaining new oxidodiperoxidomolybdates using pyridine dicarboxy acid blocks is currently in progress.

CRedit authorship contribution statement

Adrianna Sławińska: Conceptualization, Writing - original draft, Investigation, Formal analysis. **Paweł Serda**: Investigation, Formal analysis. **Marcin Oszajca**: Investigation, Formal analysis. **Katarzyna Pamin**: Investigation, Formal analysis. **Jan Połtowicz**: Investigation, Formal analysis. **Wiesław Łasocha**: Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2020.114530>.

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