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Crystal and Molecular Structures and Thermal Decomposition of Calcium(II) Complexes with Pyridine Monocarboxylic Acid *N*-oxides

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The crystal and molecular structures of three Ca(II) *N*-oxide complexes were determined by single-crystal X-ray diffraction technique and refined to R=0.033–0.082.

Catena-bis-μ-(picolinato *N*-oxido)calcium(II), [Ca(*N*-picO)$_2$], crystallized in the space group *C*2/*c*, with Z=4 and cell dimensions of a=9.662(8) Å, b=8.909(5) Å, c=14.670(31) Å and β=109.2(1)°. Catena-diaqua-μ-(nicotinato *N*-oxide)calcium(II), [Ca(N-nicO)$_2$(H$_2$O)$_2$], was monoclinic, $P2_1/c$, with Z=2 and cell dimensions of a=8.109(3) Å, b=9.479(4) Å, c=8.970(4) Å and β=97.32(3)°. Catena-diaqua-μ-(isonicotinato *N*-oxide)calcium(II), [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] had cell of dimensions a=8.013(3) Å, b=9.808(8) Å, c=8.856(5) Å and β=95.86(4)°. The space group was $P2_1/c$ with Z=2.

A highly distorted octahedral coordination geometry was observed with the Ca(II) ion in [Ca(*N*-picO)$_2$], whereas with [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] no significant deviations from ideal octahedral geometry were observed. With [Ca(*N*-picO)$_2$] coordination was observed through all three oxygen atoms of the ligand. There is a chelate coordination through the *N*-oxide oxygen atom and one carboxylic oxygen atom, while the other carboxylic oxygen atom is joined to the adjacent metal atom. The polymeric network runs parallel with the *ab*-plane. The structures of [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] are likewise polymeric. The carboxylic groups form bridges between adjacent metal ions and the polymeric network runs in the direction of *bc*-plane.

The thermal decomposition of all three complexes was also studied with the aid of thermogravimetric measurements and phase identification by IR-spectroscopy.

Pyridine monocarboxylic acid *N*-oxides coordinate in many different ways with metal ions in the solid state.[1-11] For Cu(II), polymeric structures have been described with nicotinic acid *N*-oxide.[1,2] Other divalent metal ions form polymeric species, more willingly as the ionic radius increases: for example, Cd^{2+} forms a chain polymer with isonicotinic acid *N*-oxide, in which coordination occurs through one of the carboxylic oxygen atoms and the *N*-oxide oxygen atom.[3] Likewise lead(II) ions form polymeric compounds with all three of the present monocarboxylic acid *N*-oxides.[4]

EXPERIMENTAL

The crystals of [Ca(*N*-picO)$_2$], [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] were prepared as reported earlier.[5] Details of the data collections have been summarized in

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Table 1. The data were corrected for Lorentz and polarization factors but not for absorption.

Structures were determined by direct methods (MULTAN 80)[12] and the fullmatrix least squares refinement was carried out by the X-Ray System programs.[13] Tables 3, 4 and 5 present the final atomic coordinates and U_{eq} parameters with their standard deviations for all three compounds. The difference Fourier map gave the coordinates of all hydrogen atoms and they were then refined with isotropic temperature factors. Lists of the structure factors and anisotropic thermal parameters are available from the authors upon request.

The IR spectra were run on Perkin-Elmer 283 IR spectrometer and the TG curves on a Perkin-Elmer TGS-2 thermogravimetric system.

RESULTS AND DISCUSSION

Description of the structures. The labeling and the structure of the molecules are given in Fig. 1 for [Ca(*N*-picO)$_2$], in Fig. 2 for [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and Fig. 3 for [Ca(*N*-inicO)$_2$(H$_2$O)$_2$]. The structures of all three complexes can be described as polymeric networks.

The coordination spheres of the central metal ions of the complexes are presented in Fig. 4. Coordination around the calcium(II) ions is octahedral with Ca−O bond lengths varying between 2.251(1) and 2.387(1) Å. Other octahedral calcium complexes show similar values.[14–20]

Polymeric sheet of [Ca(*N*-picO)$_2$] are formed by coordination of carboxylic oxygens (O2) and (O3) with adjacent metal ions. The oxygens (O1) of the N−O group occupy the remaining axial positions to form a distorted octahedral coordination sphere. Thus, a polymeric network is formed which is parallel to the *ab*-plane of the unit cell. The plane of the *N*-oxide heterocycle forms an angle of 91.2° with the plane formed by the metal network.

Table 1. Crystal and collection data.

	[Ca(*N*-picO)$_2$]	[Ca(*N*-nicO)$_2$(H$_2$O)$_2$]	[Ca(*N*-inicO)$_2$(H$_2$O)$_2$]
FW	316.28	352.31	352.31
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.662(8)	8.109(3)	8.013(3)
b	8.909(5)	9.479(4)	9.808(8)
c	14.670(31)	8.970(4)	8.856(5)
β (°)	109.2(1)	97.32(3)	95.86(4)
V (Å)	1192	683.8	692.5
Z	4	2	2
D_c	1.76	1.71	1.69
Radiation	MoK_α (graphite-monochromated, λ=0.71069 Å)		
Diffractometer	SYNTEX P2$_1$		
Scan mode	$\theta/2\theta$	ω	$\theta/2\theta$
2θ max(°)	60	60	60
Reflections used in the refinement	1033	1287	1528
$R=\frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$	0.082	0.033	0.034
μ(MoK_α)(cm^{-1})	5.46	4.97	4.91

Table 2. Selected bond distances and angles involving the ligands.

	[Ca(*N*-picO)$_2$]	[Ca(*N*-nicO)$_2$(H$_2$O)$_2$]	[Ca(*N*-inicO)$_2$(H$_2$O)$_2$]
O1–N1	1.292(6)	1.334(1)	1.331(1)
O2–C6	1.241(7)	1.244(1)	1.242(1)
O3–C6	1.258(6)	1.247(1)	1.242(1)
C6–C(ring)	1.520(6)	1.514(1)	1.506(1)
N1–O1–Ca	140.4(3)		
C6–O2–Ca	139.6(3)	153.2(1)	161.1(1)
C6–O3–Ca	170.5(4)	172.7(1)	153.1(1)
O2–C6–O3	123.6(4)	125.6(1)	125.7(1)

Table 3. Fractional coordinates of [Ca(*N*-picO)$_2$] with estimated standard deviations in parenthesis and temperature factors U_{eq} ($U_{eq}=100\cdot(U_{11}+U_{22}+U_{33})/3$).

Atom	*x*	*y*	*z*	U_{eq}
Ca(1)	0.0000(0)	0.1360(1)	0.2500(0)	1.94
O(1)	0.0178(5)	0.1597(4)	0.4081(2)	5.06
O(2)	−0.1615(4)	0.3202(4)	0.2603(2)	3.87
O(3)	−0.3218(4)	0.4599(4)	0.2990(3)	3.93
N(1)	−0.0255(5)	0.2462(5)	0.4640(3)	3.12
C(1)	0.0365(6)	0.2318(6)	0.5596(3)	3.42
C(2)	−0.0003(6)	0.3158(6)	0.6251(3)	3.36
C(3)	−0.1130(6)	0.4171(6)	0.5920(3)	3.66
C(4)	−0.1806(6)	0.4338(6)	0.4935(3)	3.05
C(5)	−0.1386(5)	0.3487(5)	0.4282(3)	2.48
C(6)	−0.2106(5)	0.3765(5)	0.3207(3)	2.69
H(1)	0.1134(65)	0.1815(68)	0.5772(42)	5.72
H(2)	0.0377(46)	0.2971(47)	0.6934(30)	2.26
H(3)	−0.1580(71)	0.4587(74)	0.6340(46)	6.25
H(4)	−0.2699(48)	0.4965(50)	0.4653(29)	1.83

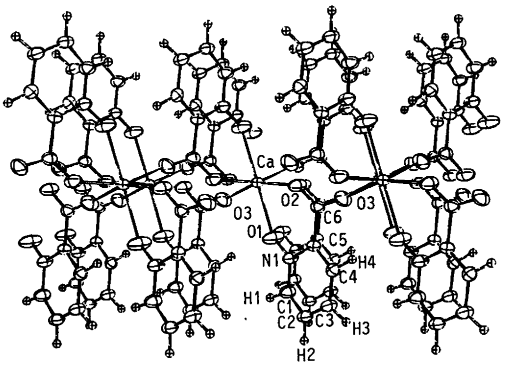


Fig. 1. The network of [Ca(*N*-picO)$_2$] including the atomic labeling.

Table 4. Fractional coordinates of [Ca(N-nicO)$_2$(H$_2$O)$_2$] with estimated standard deviations in parenthesis and temperature factors U_{eq} ($U_{eq}=100\cdot(U_{11}+U_{22}+U_{33})/3$).

Atom	x	y	z	U_{eq}
Ca(1)	0.0000(0)	0.0000(0)	0.0000(0)	1.28
O(1)	−0.4370(1)	0.1103(1)	−0.7997(1)	2.71
O(2)	0.0096(1)	0.1103(1)	−0.2268(1)	2.66
O(3)	−0.0287(1)	0.2856(1)	−0.3910(1)	2.46
O(4)	−0.2924(1)	0.0128(1)	−0.0408(1)	2.91
N(1)	−0.3616(1)	0.0520(1)	−0.6738(1)	2.05
C(1)	−0.3946(1)	−0.0843(1)	−0.6400(1)	2.67
C(2)	−0.3188(1)	−0.1432(1)	−0.5098(1)	2.77
C(3)	−0.2073(1)	−0.0658(1)	−0.4119(1)	2.30
C(4)	−0.1759(1)	0.0738(1)	−0.4483(1)	1.77
C(5)	−0.2549(1)	0.1301(1)	−0.5800(1)	1.98
C(6)	−0.0555(1)	0.1641(1)	−0.3465(1)	1.75
H(1)	−0.4582(45)	−0.1433(18)	−0.7336(22)	28.99
H(2)	−0.3546(17)	−0.2415(10)	−0.4885(11)	3.94
H(3)	−0.1452(16)	−0.1135(9)	−0.3253(11)	3.26
H(4)	−0.2360(13)	0.2217(8)	−0.6145(10)	2.27
H(5)	−0.3796(22)	−0.0343(13)	−0.1014(14)	6.91
H(6)	−0.3344(22)	0.0527(12)	0.0324(17)	6.78

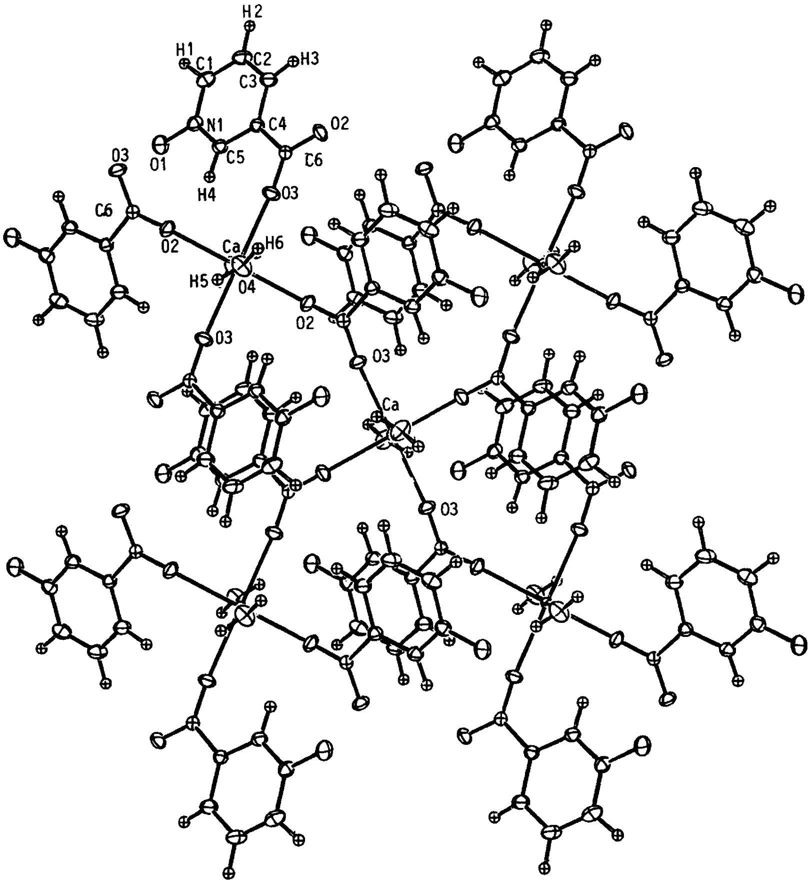


Fig. 2. The network of [Ca(N-nicO)$_2$(H$_2$O)$_2$] including the atomic labeling.

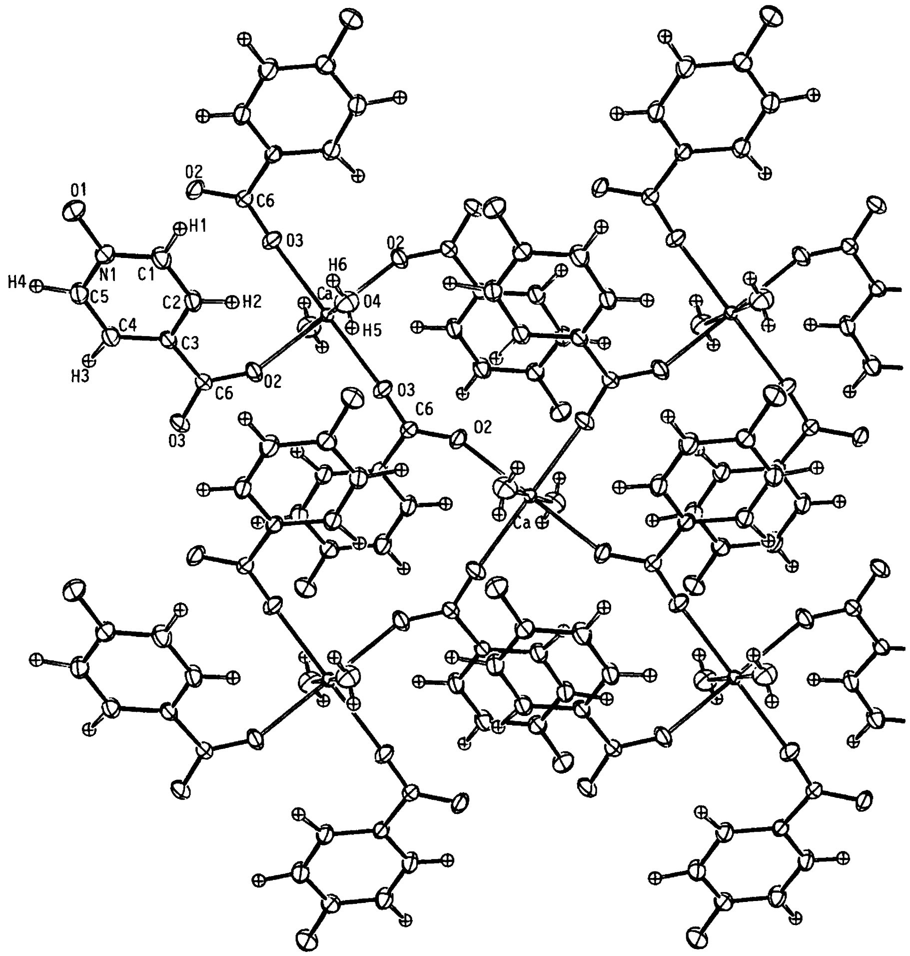


Fig. 3. The network of $[Ca(N\text{-}inicO)_2(H_2O)_2]$ including the atomic labeling.

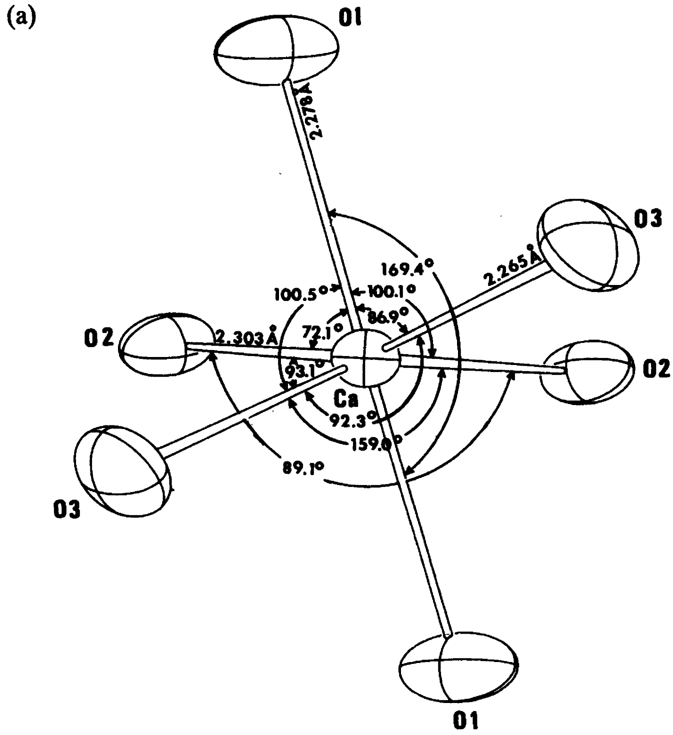
The O2–Ca–O1 angle is 72.1(1)° whereas in corresponding picolinic acid *N*-oxide complexes it varies from 90.2 to 97.2°.[5] The angle N1–O1–Ca of 140.4(3)° deviates markedly from other corresponding angles, which vary between 120.9 and 116.1°.[5] These distortions may be ascribed to the propensity of the picolinic acid *N*-oxide anion towards chelation via the *N*-oxide oxygen in aqueous solution.

The angle O2–C6–O3 of the carboxylate group is 123.6(4)°. This deviates only slightly from the theoretical angle of 120° and from the corresponding angle in other metal complexes of picolinic acid *N*-oxide.[5] The O1–N1 bond distance of 1.292(6) Å in $[Ca(N\text{-}picO)_2]$ is remarkably short compared to the O1–N1 bond of $[M(N\text{-}picO)_2(H_2O)_2]$, where for $M=Mn^{2+}$, Co^{2+}, Ni^{2+} and Cu^{2+} this same bond length varies between 1.329 and 1.341 Å.[5]

The structures of the complexes $[Ca(N\text{-}nicO)_2(H_2O)_2]$ and $[Ca(N\text{-}inicO)_2(H_2O)_2]$ are very similar. The coordination spheres (Fig. 4) are almost undistorted octahedra. The axial positions are occupied by aqua ligands and the carboxylic oxygens (O2 and O3) are in the

Table 5. Fractional coordinates of [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] with estimated standard deviations in parenthesis and temperature factors U_{eq} ($U_{eq}=100\cdot(U_{11}+U_{22}+U_{33})/3$).

Atom	*x*	*y*	*z*	U_{eq}
Ca(1)	0.0000(0)	0.0000(0)	0.0000(0)	1.39
O(1)	0.4661(1)	−0.5804(0)	0.2830(0)	2.93
O(2)	0.0230(1)	−0.3641(0)	−0.2941(0)	2.86
O(3)	0.0614(1)	−0.1781(0)	−0.1542(0)	2.90
O(4)	0.2901(1)	0.0599(1)	0.0352(1)	2.93
N(1)	0.3819(1)	−0.5148(0)	0.1677(1)	2.20
C(1)	0.2813(1)	−0.5862(1)	0.0642(1)	2.45
C(2)	0.1891(1)	−0.5194(1)	−0.0531(1)	2.30
C(3)	0.1966(1)	−0.3784(1)	−0.0637(1)	1.88
C(4)	0.3051(1)	−0.3095(1)	0.0417(1)	2.39
C(5)	0.3972(1)	−0.3782(1)	0.1557(1)	2.57
C(6)	0.0847(1)	−0.3006(1)	−0.1806(1)	2.00
H(1)	0.2719(8)	−0.6908(7)	0.0846(7)	3.82
H(2)	0.1025(9)	−0.5812(7)	−0.1206(8)	5.01
H(3)	0.3102(8)	−0.2150(6)	0.0369(7)	2.61
H(4)	0.4856(9)	−0.3269(7)	0.2311(8)	4.39
H(5)	0.3282(11)	0.0743(8)	−0.0326(10)	5.20
H(6)	0.3507(11)	0.0298(9)	0.0926(10)	6.15



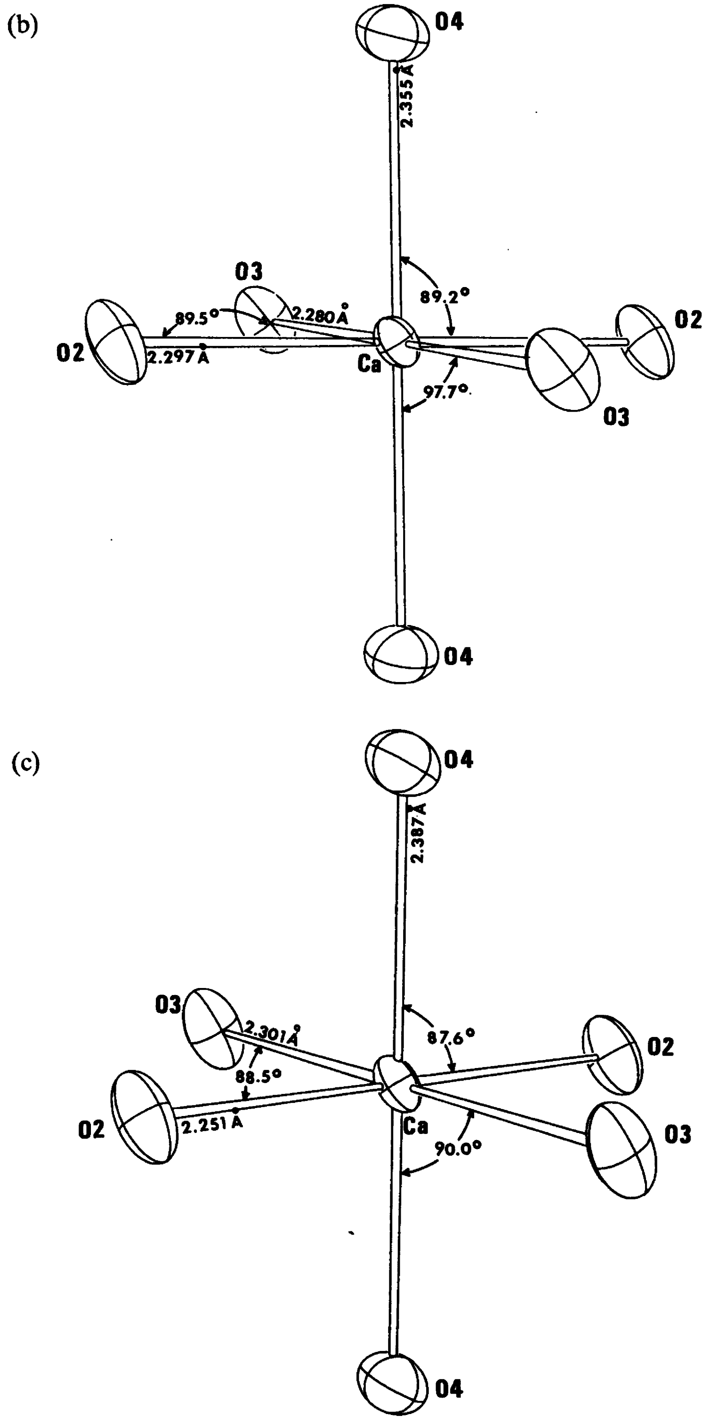


Fig. 4. The coordination octahedron of a) [Ca(*N*-picO)$_2$], b) [Ca(*N*-nicO)$_2$(H$_2$O)$_2$], c) [Ca(*N*-inicO)$_2$(H$_2$O)$_2$].

Table 6. The hydrogen bonding system in $[Ca(N\text{-nicO})_2(H_2O)_2]$ and in $[Ca(N\text{-inicO})_2(H_2O)_2]$.

	A−H···B	A−H(Å)	H···B(Å)	A···B(Å)	∠AHB(°)
$[Ca(N\text{-nicO})_2(H_2O)_2]$	O4−H5···O1[a]	0.947(15)	1.783(15)	2.724(1)	172(2)°
	O4−H6···O1[b]	0.865(16)	1.892(7)	2.749(1)	171(1)
$[Ca(N\text{-inicO})_2(H_2O)_2]$	O4−H5···O1[c]	0.715(9)	2.064(9)	2.768(1)	168(1)°
	O4−H6···O1[d]	0.729(9)	2.051(9)	2.768(1)	168(1)°

Symmetry codes: [a] $-x-1,\ -y,\ -z-1$. [b] $x,\ y,\ z+1$. [c] $x,\ -y-\frac{1}{2},\ z-\frac{1}{2}$. [d] $-x+1,\ y+\frac{1}{2},\ -z+\frac{1}{2}$.

equatorial positions. A 2-dimensional polymeric sheet is thus formed by the bridging carboxylic oxygens which is parallel to the *bc*-plane. The N−O oxygen atoms do not coordinate with the Ca as in the picolinato structure. Here, in combination with aqua ligands from neighboring sheets, the N−O oxygen atoms participate in a hydrogen bonding system which serves to interconnect these neighboring systems into an extensive three dimensional network. The hydrogen bond systems of $[Ca(N\text{-nicO})_2(H_2O)_2]$ and $[Ca(N\text{-inicO})_2(H_2O)_2]$ are presented in Table 6.

The angle between the plane of the pyridine *N*-oxide and the plane formed by the metal Ca atoms is 48.9° for $[Ca(N\text{-nicO})_2(H_2O)_2]$ and 48.5° for $[Ca(N\text{-inicO})_2(H_2O)_2]$. The

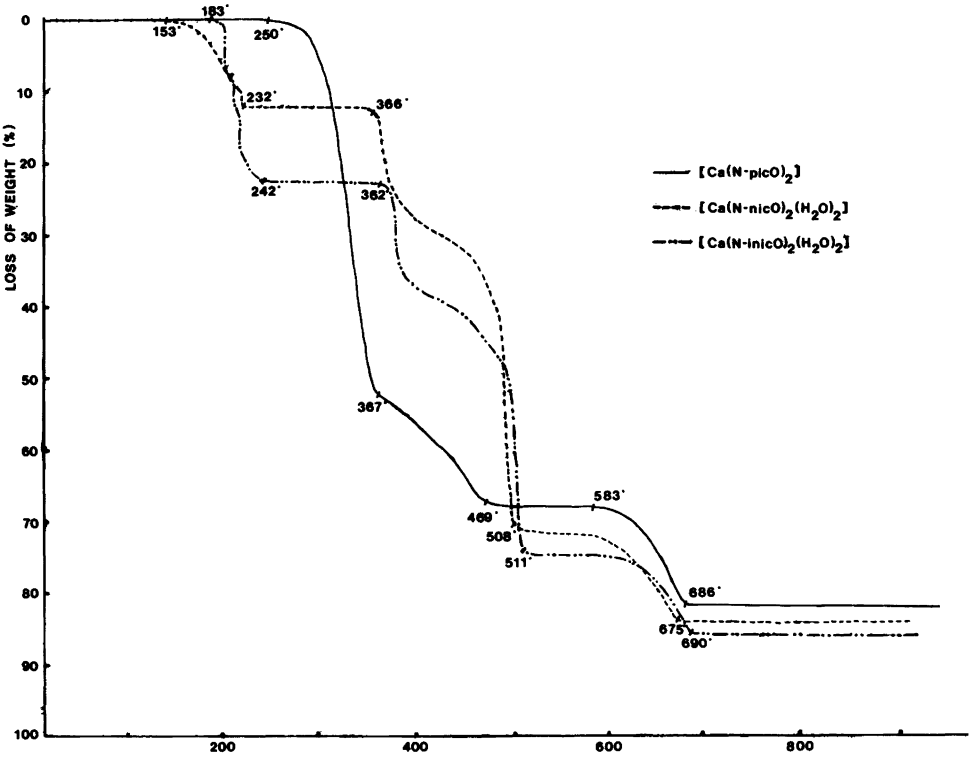


Fig. 5. TG curves of the complexes. Pt pan was used with samples of 8.0−9.5 mg. Heating rate was 5°/min, air flow 45 ml/min.

O4–O4′ contact distances are 3.544(1) Å in [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and 3.677(1) Å in [Ca(*N*-inicO)$_2$(H$_2$O)$_2$].

The angles of the carboxylate groups are 125.6(1)° for [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and 125.7(1)° [Ca(N-inicO)$_2$(H$_2$O)$_2$]. Coordination does not cause any noticeable opening compared with the angle of 125.2° in the free acid.

Thermogravimetric study. The TG curves of the complexes are presented in Fig. 5. The mechanism of thermal decomposition of the complexes was studied by running the IR-spectra of all stable intermediates. In all three complexes the main step of the decomposition is a conversion via calcium carbonate to calcium oxide, after the loss of the aqua ligands in nicotinato *N*-oxide and isonicotinato *N*-oxide complexes. This feature can be seen in the IR-spectra with rise in temperature.

The decomposition of [Ca(*N*-picO)$_2$] begins at 250 °C and continues till 469 °C, corresponding to the compustion of the organic material. The plateau between 469 and 583 °C corresponds to the CaCO$_3$ intermediate (calculated 31.6 % and observed 32 %). The final decomposition begins at 583 °C and the CaO level is reached by 686 °C.

The decomposition of [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] begins at 153 °C with the loss of two aqua ligands. The theoretical weight loss of two water molecules is 10.2 % and observed 10 %. The intermediate that forms is stable until 366 °C.

The IR-spectrum run on this intermediate shows changes in the M–O frequency region (850–500 cm^{-1}), H–O–H bending mode (1600–1630 cm^{-1}) and OH stretchings (3550–3200 cm^{-1}) due to the loss of aqua ligands. The interesting change is in the frequency of the N–O oxygen, which increases from 1220 to 1242 cm^{-1} during the water releasing process. The increase is due to the breaking of the hydrogen bonds between N–O oxygen and aqua ligands. The central metal ion in this intermediate is most probably four-coordinated, without the N–O coordination. The further decomposition begins at 366 °C and continues in two steps without stable intermediates until 508 °C when the CaCO$_3$ level is reached (calculated 28.4 % and observed 28 % of total weight).

In spite of the structural similarity of [Ca(*N*-nicO)$_2$(H$_2$O)$_2$] and [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] the thermal properties of these two complexes deviate greatly. A violent decomposition of [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] has been reported in an earlier publication,[21] and precautions were taken to avoid this by a gentle grinding of the sample. The fast exothermic decomposition of the isonicotinate *N*-oxide complex shows it to be less stable than the other two complexes studied. The decomposition of [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] begins with the loss of two aqua ligands at 183 °C continuing immediately to a plateau at about 26 % weight loss. The intermediate formed is stable between 242 and 362 °C. The IR-spectrum of the intermediate shows clearly the disappearance of the aqua ligand absorptions, but other changes are difficult to detect. The thermal decomposition of [Ca(*N*-inicO)$_2$(H$_2$O)$_2$] continues from 362 °C very similarly to that of [Ca(*N*-nicO)$_2$(H$_2$O)$_2$], reaching the plateaus for CaCO$_3$ and CaO at about the same temperatures.

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