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Solid state coordination chemistry of pyridinedicarboxylic acid isomers. III Synthesis and crystal structures of complexes of Zn and Ni with lutidinic acid (lutidinic = 2,4-pyridinedicarboxylic)

Elsa E. Sileo[a,*], Alexandre S. de Araujo[b], Graciela Rigotti[c], Oscar E. Piro[c], Eduardo E. Castellano[b]

[a]*Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pab. II, 1428EHA, Buenos Aires, Argentina*

[b]*Instituto de Física de São Carlos, Universidade de São Paulo, C.P. 369, 13560 São Carlos (SP), Brazil*

[c]*Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata and Instituto de Física de La Plata (CONICET), C.C. 67, 1900 La Plata, Argentina*

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Abstract

The synthesis and the crystal and molecular structures of three metal(II) derivatives of lutidinic acid are presented (lutidinic acid = 2,4-pyridinedicarboxylic acid = $H_2$2,4-pydc). Zn(2,4-pydc)$(H_2O)_4]\cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$, with $a = 7.764(3)$, $b = 6.546(3)$, $c = 22.021(8)$ Å; $\beta = 91.45(4)°$; and $Z = 4$. Na_2[Zn(2,4-pydc)$_2$($H_2O)_2]\cdot 8H_2O$ crystallizes in $P2_1/a$, with $a = 7.070(2)$, $b = 13.630(2)$, $c = 12.520(1)$ Å; $\beta = 91.66(1)°$; and $Z = 2$. $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ crystallizes in the triclinic space group $P-1$, with $a = 5.200(7)$, $b = 7.890(3)$, $c = 13.872(5)$ Å; $\alpha = 84.96(3)$, $\beta = 85.64(2)°$, $\gamma = 73.21(4)$; and $Z = 2$. The Zn and Ni ions are hexacoordinated and the lutidinate group is almost planar binding the metal through an oxygen atom from the 2-carboxylate group. All compounds present a dangling uncoordinated 4-carboxylate group. The stereochemistry of the title compounds is compared with other metal (II) pyridinedicarboxylates.

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Keywords: Crystal structure; Zinc; Nickel; Lutidinate; 2,4-pyridinedicarboxylate

1. Introduction

The series of the pyridinedicarboxylic acids (H_2pydc) includes the 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridinedicarboxylic isomers, which form 1:1 and 1:2 metal derivatives that may exhibit various coordination geometries. The relative position of the coordinating atoms (vg. O and N) determines planar structures that lead to molecular solids, as in some 2,6- [1,2] and 2,4-pyridinedicarboxylate [3] derivatives, or may present deviations from planarity that lead to two- [4] or three-dimensional [4,5] structures.

* Corresponding author. Tel.: +11-4576-3358; fax: +11-4576-3341.

E-mail address: sileo@qi.fcen.uba.ar (E.E. Sileo).

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In particular, interest in the 2,4-pyridinedicarboxylic acid (lutidinic acid) derivatives centres on its biological activities as a immune-suppressive and fibro-suppressive compound [6], that shows effects on the growth and floral induction of certain species [7,8], and it protects certain enzymes from cells of *Bacillus subtilis* from heat inactivation [9,10]. As the role played by lutidinic acid in these processes is not truly understood, the study of its coordination chemistry with biologically important transition metal ions, may be explored as structural models in biological systems. So far, crystal and molecular structures are reported only for $Na_2[Cu(2,4\text{-pydc})_2(H_2O)]\cdot 2H_2O$ [3] and $K_3[VO(O_2)(2,4\text{-pydc})]\cdot 3.25\ H_2O$ [11]. In this paper, we report the synthesis and the crystal and molecular structures of the first Zn(II) 1:1 and 1:2 lutidinates and the first Ni(II) 1:1 lutidinate.

2. Experimental section

2.1. Materials and methods

The lutidinic acid ligand, as monohydrate (Aldrich Chemical Company), and the other reagents were used as provided. The metal contents of the solids were determined at INQUIMAE, Universidad de Buenos Aires, with a Varian Techtrom A-A5R atomic absorption spectrometer. Elemental analyses were performed in a Carlo Erba EA 1108 microanalyser. The X-ray diffraction data were collected at 293(2) K in an Enraf-Nonius CAD-4 working in the ω-2θ scanning mode.

2.2. Synthesis of the solids

$[Zn(2,4\text{-pydc})(H_2O)_4]\cdot H_2O$ (**1**). NaOH solution (4.2 ml, 0.952 M, 4 mmol) was added to an aqueous suspension of 2,4-pyridinedicarboxylic acid monohydrated (175 ml, 0.370 g, 2.0 mmol). After stirring for 30 min, $ZnSO_4$ solution (20 ml, 0.1 M, 2 mmol) was added (final pH was 4.04). Found: C, 27.0; H, 4.2; N, 4.2; Zn, 20.4. Calc. for $C_7H_{13}NO_9Zn$: C, 26.8; H, 4.1; N, 4.4; Zn, 20.4.

$Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ (**2**). The solid was prepared similarly by adding NaOH solution (2.1 ml, 0.952 M, 2 mmol) to an aqueous suspension of pyridine-2,4-dicarboxylic acid monohydrated (175 ml, 0.370 g, 2.0 mmol). After stirring for 30 min, a $ZnSO_4$ solution (10 ml, 0.1 M, 1 mmol) was added (final pH was 4.5). Found: C, 27.1; H, 4.3; N, 4.4; Na, 7.4; Zn, 10.3. Calc. for $C_{14}H_{26}N_2O_{18}ZnNa_2$: C, 27.0; H, 4.2; N, 4.5; Na, 7.4; Zn, 10.5.

$[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**). $NiSO_4\cdot 6H_2O$ (0.5256 g, 2 mmol) was added to an aqueous suspension of 2,4-pydc acid (180 ml, 0.334 g, 2 mmol). NaOH solution (0.1 N) was added with stirring at 80 °C, final pH at 298 K was 4.21. Found: C, 28.2; H, 3.8; N, 4.7; Ni, 19.5. Calc. for $C_{14}H_{22}N_2O_{16}Ni_2$: C, 28.4; H, 3.7; N, 4.7; Ni, 19.8.

In all cases, the solids were obtained by slow evaporation of the solutions at 298 K. The complexes were stable in air and insoluble in water and ethanol. The zinc derivatives were colourless and the nickel derivative was clear green.

2.3. Data collection and processing

Details in common. Programs used for data reduction was XCAD-4 [12]. Data were corrected for absorption effects according to Walker and Stuart [13], for compound **1** and to Spek [14], for **2** and **3**. The structures were solved and refined using the SHELXS-93 [15] and SHELXL-93 [16], respectively.

$[Zn(2,4\text{-pydc})(H_2O)_4]\cdot H_2O$ (**1**). It was not possible to find single crystals in the sample batch with good diffraction conditions. A first sample measured with Mo Kα radiation, from which the crystal structure was solved, refined anisotropically to an $R1$-factor of 12.7%. A second sample was mounted on a diffractometer provided with Cu Kα radiation. Although it was apparent, that it was also composed by more than one moiety, judicious elimination of a few reflections allowed the selection of a single crystal unity from which a complete data collection was performed. The refinement converged to $R1 = 0.077$. Numerical absorption corrections did not improved significantly this figure, possibly because the crystal faces defining the boundary of the crystal did not correspond to those bounding the measured diffracting unity. Because of this fact and since the crystal had dimensions small enough to complain with the hypothesis of the procedure, an empirical absorption correction was applied after

which the anisotropic refinement dropped the agreement factor to a final $R1$ value of 4.6%.

All hydrogen atoms were located in a difference Fourier map. The ones belonging to the 2,4-pyridinedicarboxylate ligand were positioned stereo-chemically and refined with the riding model. The waters H-atoms were refined isotropically.

$Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ (**2**). The samples were thin crystal plates that diffracted poorly. For data up to 0.757 Å resolution, only 58% of the X-ray intensities were above two standard deviations of measurement errors. A difference Fourier map phased on most non-H atoms showed two peaks 0.89 Å apart and 3.3 and 2.7 e $Å^{-3}$ high. This residual electron density was modelled during the final refinement in terms of a disordered water molecule filling the two sites with occupancies that added to one and a common isotropic displacement parameter. All H-atoms of the dipicolinate ligand were found in a Fourier map. However, they were positioned stereochemically and refined with the riding model. Water hydrogen atoms could not be located reliably and therefore they were not included in the final refinement.

$[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**). All hydrogen atoms were found among the first 11 peaks of a difference Fourier map. However, the ligand H-atoms were refined as described above for the other complexes. The water H-atoms were included in the final molecular model at their found positions and refined with a common isotropic displacement parameter.

3. Results and discussion

Structural data for the compounds were obtained by least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 18 reflections in the $21.12 < \theta < 56.32°$ (Cu Kα) range for **1**, 25 reflections in the $11.6 < 2\theta < 18.99°$ (Mo Kα) range for **2** and 25 reflections in the $22.76 < \theta < 43.59°$ (Cu Kα) range for **3**. Experimental details are given in Table 1.

3.1. Description of the structure of the complexes

$Zn(2,4\text{-pydc})(H_2O)_4\cdot H_2O$ (**1**). The coordination environment of Zn(II) ion is shown in the ORTEP [17] drawing of Fig. 1. Selected distances and angles are shown in Table 2. The zinc is equatorially coordinated to a lutidinate ion, acting as a bidentate ligand through its nitrogen and one oxygen atom from the 2-carboxylate group (distances Zn–N = 2.099(2), Zn–O(1) = 2.081(2) Å), and to two water molecules (distances Zn–O(1W) = 2.070(2) and Zn–O(3W) = 2.095(2) Å). The axial positions are occupied by two water molecules [distances Zn–O(2W) = 2.210(2) and Zn–O(4W) = 2.101(2) Å]. *cis* angles around Zn(II) are in the range from 77.98(9) to 97.9(1)° and *trans*angles vary from 169.10(9) to 174.15(8)°. The zinc ion is slightly out (0.086(1) Å) of the equatorial plane of ligands towards the nearest axial ligand (O(4W)).

The pyridine ring departs from coplanarity, the carboxylate O(1)–C(6)–O(2) bonded to zinc, and O(4)–C(7)–O(3) are rotated 3.5(6) and 9.7(2)°, respectively, from the organic ring. None of the two oxygen atoms from the 4-carboxylate group are bonded to the metal ion forming a pendant $-RCOO^-$ group. All lutidinate groups are symmetry related and lie approximately in *ab*-planes displaying an alternated arrangement that does not show π–π interactions. Distance between aromatic planes is 3.3 Å. The pendant carboxylate forms an inter-molecular hydrogen bond involving a coordinated water molecule (O(1W), donor) and one oxygen atom (O′(3), acceptor); these hydrogen bonds link the aromatic ring from different sheets.

The lattice is further stabilized by a net of OW–H···O and OW–H···OW hydrogen bonds involving O(3W), O(4W) and the crystallization water molecule O(5W). This interaction determines the formation of a zigzag chain, formed by Zn–O(3W)–O(4W)–Zn links that run along the *b*-axis. Fig. 2 shows the packing of compound **1**, along the *a*-axis and the chains along *b*.

Bond lengths C–O in the coordinated 2-carboxylate differ from those of the pendant 4-carboxylate. Distance C(6)–O(2) = 1.238(3) Å is shorter than distance C(6)–O(1) = 1.273(4) Å, this fact is attributable to a marked double bond character of C(6)–O(2) bond. Distances in the 4-carboxylate, C(7)–O(3) and C(7)–O(4) are similar (1.267 and 1.245 Å), respectively; this may be attributable to the fact that the carboxylate in the 4-position is not coordinated to Zn.

Table 1
Crystallographic data for $[Zn(2,4\text{-pydc})(H_2O)_4]\cdot H_2O$ (**1**), $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ (**2**) and $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**). ($R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$)

	Compound **1**	Compound **2**	Compound **3**
Empirical formula	$C_7H_{13}NO_9Zn$	$C_{14}H_{26}N_2O_{18}ZnNa_2$	$C_7H_{11}NO_8Ni$
Formula weight	320.45	621.72	295.85
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/a$	$P-1$
a (Å)	7.764(3)	7.070(2)	5.200(7)
b (Å)	6.546(3)	13.630(2)	7.890(3)
c (Å)	22.021(8)	12.520(1)	13.872(5)
α (°)	–	–	84.96(3)
β (°)	91.45(4)	91.66(1)	85.64(2)
γ (°)	–	–	73.21(4)
V (Å^3)	1118.8(8)	1206.1(4)	542.1(1)
Z	4	2	2
ρ_{calc} (mg/m^3)	1.903	1.712	1.813
μ (mm^{-1})	3.517 (Cu Kα)	1.143 (Mo Kα)	2.952 (Cu Kα)
λ (Å)	1.54184	0.71073	1.54184
$R[I > 2\sigma(I)](R_1, wR_2)$	0.046, 0.124	0.052, 0.145	0.030, 0.092
GOF	1.138	1.017	0.979
Largest diff. peak (e Å^3)	0.58	0.99	0.46
Largest diff. hole (e Å^3)	−0.67	−0.54	−0.40

$Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ (**2**). Fig. 3 shows a drawing of the compound. Selected bond distances and angles are shown in Table 2.

The zinc ion is sited on a crystallographic inversion centre, having a distorted octahedral environment. The central ion is equatorially coordinated to a symmetry related pair of lutidinate groups that act as bidentated ligands through their nitrogen atom [distance Zn–N = 2.096(3) Å] and one oxygen atom of the adjacent 2-carboxylate group [distance Zn–O(1) = 2.067(3) Å. The axial ligand is a water molecule (distance Zn–O(1W) = 2.180(3) Å). The coordination sphere is not so distorted like in the 1:1 compound and *cis* angles around Zn(II) are in the range from 79.3(1) to 91.1(1)°.

As in the case of $Zn(2,4\text{-pydc})(H_2O)_4\cdot H_2O$, the pyridine ring is nearly coplanar with the 2-carboxylate

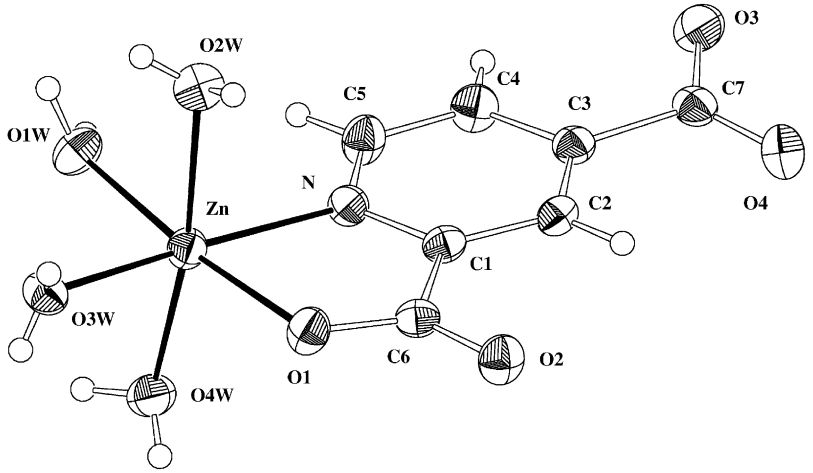

Fig. 1. Molecular plot of $Zn(2,4\text{-pydc})(H_2O)_4\cdot H_2O$ showing the numbering scheme of the non-H atoms and their displacement ellipsoids at 50% probability level. The crystallization water molecule O(5W) is not shown.

Table 2
Selected bond distances (Å) and angles (°) around zinc in $[Zn(2,4\text{-pydc})(H_2O)_4]\cdot H_2O$ (**1**) and $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ (**2**)

Bond	Compound **1**	Bond	Compound **2**
Zn–O(1)	2.081(2)	Zn–O(1)	2.067(3)
Zn–N	2.099(2)	Zn–N	2.096(3)
Zn–O(1W)	2.070(2)	Zn–O(1W)	2.180(3)
Zn–O(2W)	2.210(2)		
Zn–O(3W)	2.095(2)		
Zn–O(4W)	2.101(2)		
Angle	Compound **1**	Angle	Compound **2**
O(1)–Zn–N	77.98(9)	O(1)–Zn–N	79.3(1)
O(1)–Zn–O(2W)	89.83(9)	O(1)–Zn–O(1W)	91.0(1)
N–Zn–O(2W)	90.10(9)	N–Zn–O(1W)	91.1(1)
O(1)–Zn–O(3W)	92.22(9)	O(1)–Zn–N′	100.7(1)
O(1)–Zn–O(4W)	96.69(9)	O(1)–Zn–O(1W′)	89.0(1)
N–Zn–O(4W)	95.63(9)	N–Zn–O(1W′)	88.9(1)
O(1W)–Zn–O(1)	174.15(8)		
O(1W)–Zn–O(3W)	91.5(1)		
O(1W)–Zn–N	97.9(1)		
O(3W)–Zn–N	169.10(9)		
O(1W)–Zn–O(4W)	87.8(1)		
O(3W)–Zn–O(4W)	90.2(1)		
O(1W)–Zn–O(2W)	86.0(1)		
O(3W)–Zn–O(2W)	85.0(1)		

substituent bonded to zinc (dihedral angle of 3(1)°), however, the ring subtends an angle of 13.3(2)° with the 4-carboxylate group. The lutidinate groups lie approximately on *bc*-planes and are partially superimposed displaying $\pi-\pi$ interactions (distance between planes is 3.5 Å).

The sodium ions display an octahedral environment coordinating to five water molecules (Na···OW contacts in the range from 2.370(4) to 2.486(5) Å) and one oxygen atom, O(2) (distance Na···O(2) = 2.479(4) Å) of the carboxyl group bonded to zinc. Again, the carboxylate in 4-position

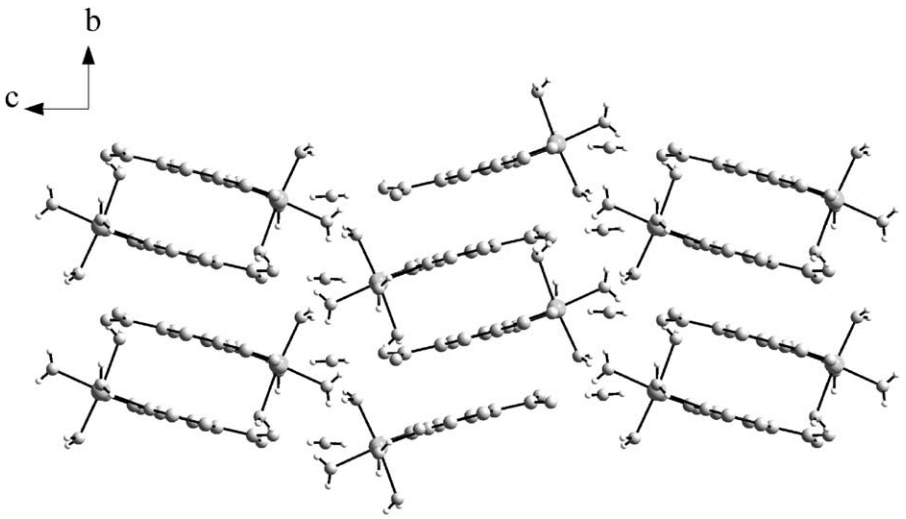

Fig. 2. Crystal packing of $Zn(2,4\text{-pydc})(H_2O)_4\cdot H_2O$ as view along the *a*-axis.

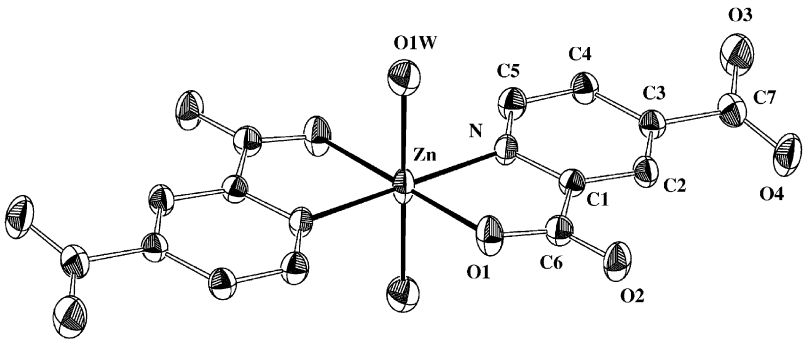

Fig. 3. Molecular plot of $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$. The interstitial water molecules O(5W) y O(6W) are not shown.

is not bounded to any of the metal ions. Bond lengths C–O in 2-carboxylate are shorter than in the pendant 4-carboxylate, compare distances C(6)–O(1) = 1.255(5) and C(6)–O(2) = 1.230(6) Å with distances C(7)–O(3) = 1.252(5) and C(7)–O(4) = 1.255(5) Å; like in the 1:1 derivative, this may be attributable to the fact that the carboxylate in the 4-position is not coordinated to a metal ion, thus it is supporting a larger electronic density.

The six-coordination of the Na ions is achieved by sharing the O(3W)-O(2W) aristae and the polyhedra form chains that run along the *a*-axis (Fig. 4). The chains are transversally connected through a net of H-bondings involving the interstitial H_2O molecules, O(5W) and O(6W).

$[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**). Structural data for the compound are listed in Tables 1 and 3. Fig. 5 is a molecular plot showing the coordination around the Ni atoms.

The compound is composed of two complex ions bridged through hydrogen bonds. Each unit cell contains two units $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$. The crystal structure is unusual in the series of the pyridinedicarboxylates and presents two Ni(II) atoms, (Ni(1) and Ni(2)), lying on different crystallographic inversion centres. Ni(1) is hexacoordinated to two water molecules and two lutidinate groups and the

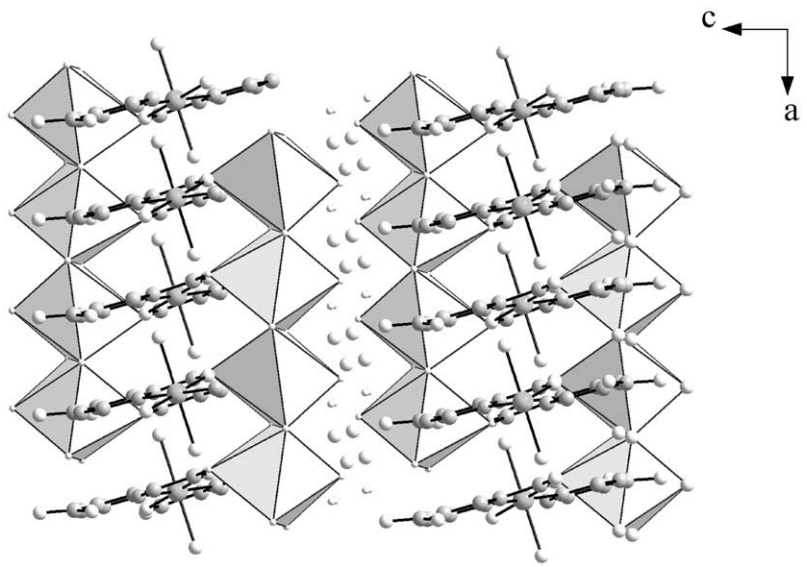

Fig. 4. Crystal packing of $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ showing the Na chains along the *a*-axis and the interstitial water molecules (some Na polyhedra are not shown).

Table 3
Selected bond distances (Å) and angles (°) in $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**)

Bond	Distance	Bond	Distance
Ni(1)–O(2)	2.054(1)	Ni(2)–O(2W)	2.095(1)
Ni(1)–N(1)	2.043(1)	Ni(2)–O(3W)	2.039(1)
Ni(1)–O(1W)	2.113(1)	Ni(2)–O(4W)	2.032(2)
C(6)–O(1)	1.237(2)	C(7)–O(4)	1.243(3)
C(6)–O(2)	1.267(2)	C(7)–O(3)	1.247(3)
Angle	Degrees	Angle	Degrees
N(1)–Ni(1)–O(2)	80.21(5)	O(4)–C(7)–O(3)	125.75(19)
N(1)–Ni(1)–O(1W)	87.91(6)	O(4W)–Ni(2)–O(3W)	88.53(7)
O(2)–Ni(1)–O(1W)	90.21(5)	O(4W)–Ni(2)–O(2W)	89.06(6)
O(1)–C(6)–O(2)	125.41(17)	O(3W)–Ni(2)–O(2W)	90.67(6)

complex carries a 2^- net charge. Ni(2) is coordinated to six water molecules and therefore the group displays a 2^+ charge. Both metallic centres are linked to each other by hydrogen bonds between O(2W) and O(4), and O(4W) and O(1). It turns out that these hydrogen bonds are unusually strong and they will be further discussed below.

Ni(1), sited on a crystal inversion centre, is equatorially coordinated to a symmetry related pair of lutidinate groups that act as bidentated ligands through their nitrogen atom (distance Ni(1)–N(1) = 2.043(1) Å) and one oxygen atom of the adjacent 2-carboxylate group (distance Ni(1)–O(2) = 2.054(1) Å). The axial ligand is a water molecule (distance Ni(1)–O(1W)) = 2.113(1) Å). Distances in the Ni(1)-polyhedron are shorter than in Zn lutidinates. The coordination sphere is less distorted that in the Zn lutidinates and the angles around Ni(II) are, N(1)–Ni(1)–O(2): 80.21° and N(1)–Ni(1)–O(W1): 87.91° (compare with angles around Zn(II) in the 1:2 compound, that are in the range from 79.3(1) to 91.1(1)°).

Ni(2) is also sited on a crystallographic inversion centre. The coordination polyhedron is formed by three H_2O molecules (O(2W), O(3W) and O(4W)) and their three symmetry-related molecules. Distances around Ni(2) (Ni(2)–O(2W): 2.095(2), Ni(2)–O(3W): 2.039(2) and Ni(2)–O(4W): 2.032(2) Å), and angles (O(4W)–Ni(2)–O(2W): 90.95 and O(4W)–Ni(2)–

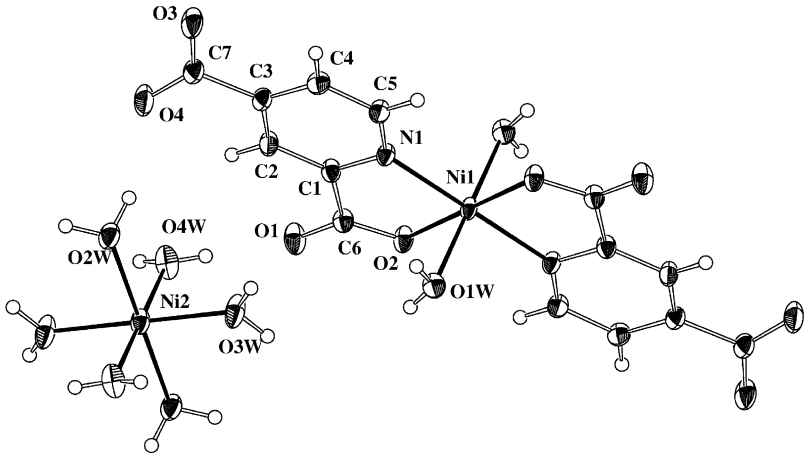

Fig. 5. Ni coordination polyhedra in $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$.

O(3W): 91.45°) reveal an almost undistorted octahedron around Ni(2).

Angles in the lutidinate ring indicate an inverse trend as the one observed in the Zn lutidinates. The measured values are as follows: plane of the aromatic ring with plane C(7)O(3)O(4)C(3), 15.2(2)°, and plane of ring with plane C(6)O(1)O(2)C(1), 6.4(2)°.

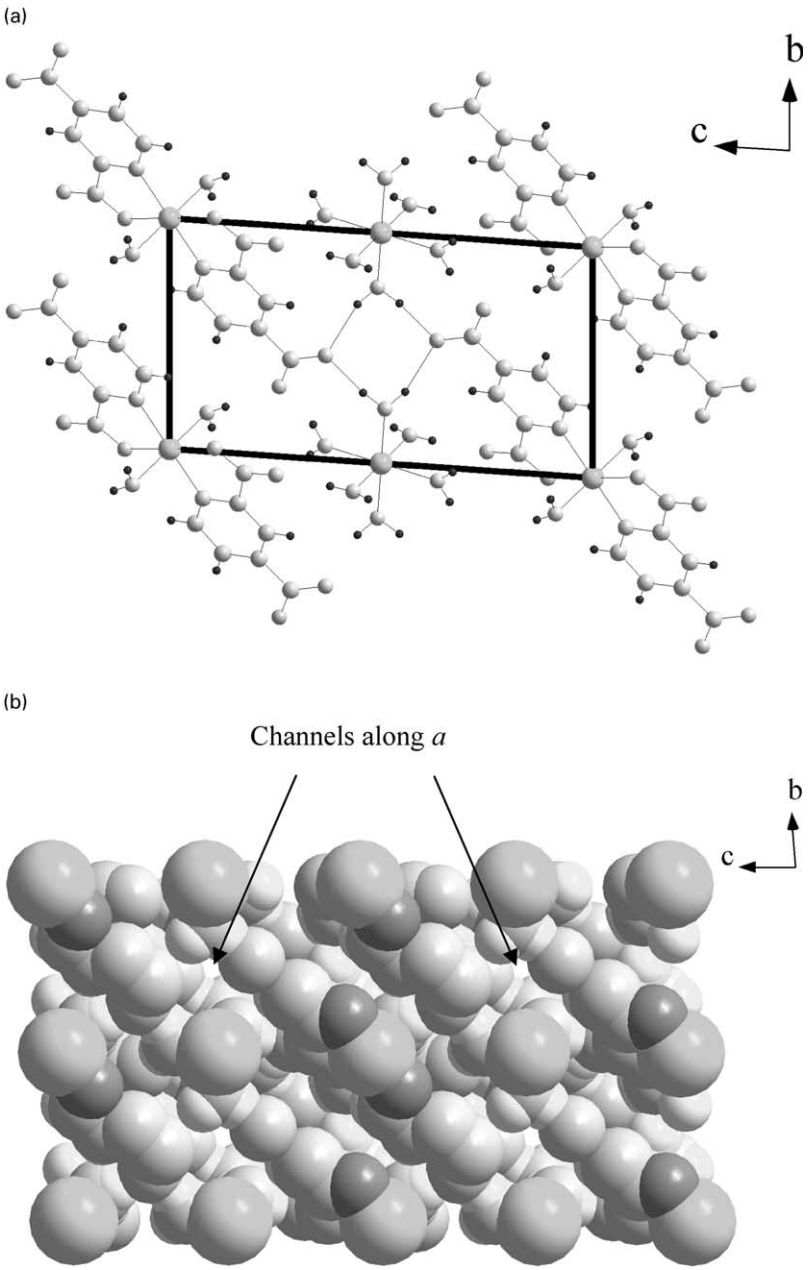

Fig. 6. (a) View of the crystal packing of $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ showing the lutidinate rings stacked along sheets parallel to (011). The strong O(2W)–H···O(4) bond is also shown. (b) A space-filling model of the crystal showing four unit cells and the channels formed along the *a*-axis.

A view of the unit cell along the *a*-axis is shown in Fig. 6. The anions Ni(2,4-pydc)$^{=}$, with the Ni(1) located at the (0,0,0) site, are stacked approximately parallel to the *bc*-plane. These sheets are intercalated with sheets formed by the $Ni(H_2O)_6^{2+}$ groups, this arrangement inhibits $\pi-\pi$ interactions between pyridinic rings. Distance between aromatic sheets is 3.2 Å.

The observed O(2W)–O(4) distance of 2.649(2) Å and the O(2W)–HW(21)–O(4) angle of 169.4(1)° reveal a strong hydrogen bond not present in other lutidinates. This interaction gives rise to a square centred arrangement of complex ions parallel to the crystal *bc*-plane. A space-filling model of the unit cell content shows the channel formed along the *a*-axis. O(4W) and O(1) oxygen atoms are also connected by H-bonds (distance O(4W)–O(1) = 2.716(2) Å, angle O(4W)–HW(41)–O(1) = 169.0(1)°).

Again, the carboxylate in 4-position is not bounded to any of the metal ions. Bond lengths C–O in 2- and 4-carboxylate differ from each other, as seen when comparing bond distances C(6)–O(1) = 1.237(2) Å and C(6)–O(2) = 1.267(2) Å of the 2-carboxylate with distances C(7)–O(3) = 1.247(3) Å and C(7)–O(4) = 1.243(3) Å in the 4-carboxylate. Like in the Zn lutidinates, the bond distances observed in the 4-carboxylate may be attributable to the fact that this carboxylate is not coordinated to a metal ion, hence supporting a larger electronic density.

The structures of three complexes described, present the carboxylate in the 2-position coordinated to the metal ion and the same dangling uncoordinated 4-carboxylate. In particular, the structure of $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]\cdot 8H_2O$ differ from the structure of the *bis*-lutidinate reported for Cu(II), $Na_2Cu(C_7NO_4H_3)_2\cdot 3H_2O$ [3], where (a) the Cu(II) is found in a square pyramidal polyhedron coordinating to two lutidinate groups and a water molecule; (b) the Na ion is coordinated to H_2O molecules and to oxygen atoms from the carboxylate in the 4-position, and (c) distance between lutidinate *bc*-planes is 3.60 Å.

These differences may be attributed to the difference in metal electronic configurations (d^9 for

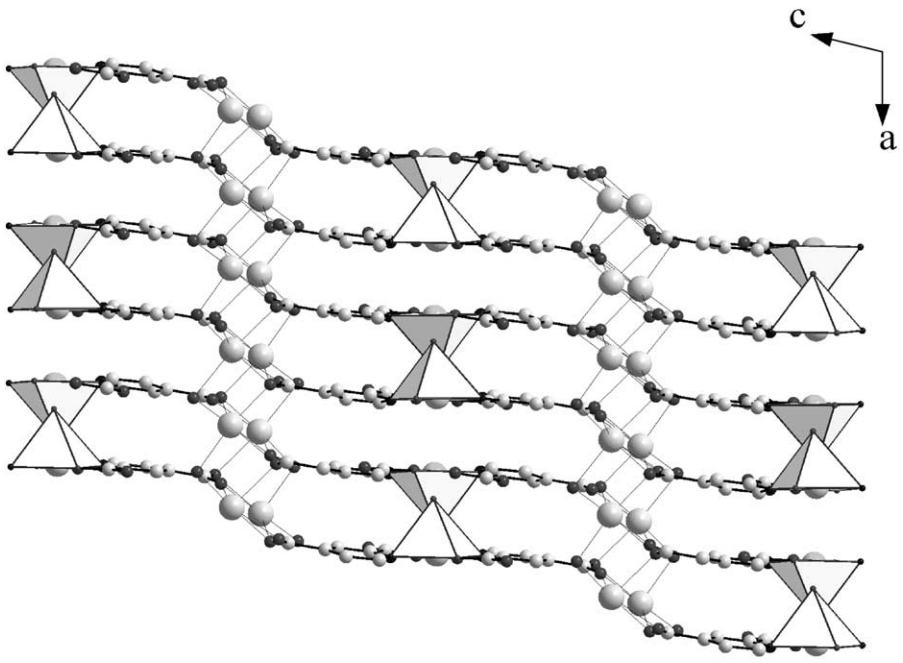

Fig. 7. Crystal packing of $Na_2Cu(2,4\text{-pydc})_2\cdot 3H_2O$ showing the pyramidal Cu(II) polyhedra staked up and down, along the *a*-direction (from Ref. [3]).

Cu(II) vs. d^{10} for Zn(II)). In $Na_2Cu(2,4\text{-pydc})_2{\cdot}3H_2O$ [3], the pyramidal Cu(II) polyhedron, usual for a d^9 ion, are staked up and down, along the *a*-direction (distance $Cu-H_2O_{apical} = 2.259(6)$ Å), this array leads to a distance of 3.60 Å between lutidinate layers (cf. Fig. 7). This large interlayer distance allows the double-bridged chain of Na ions to coordinate to the 4-carboxylate.

In $Na_2[Zn(2,4\text{-pydc})_2(H_2O)_2]{\cdot}8H_2O$, the Zn displays a slightly distorted octahedral environment with a distance $Zn-O(1W)_{axial} = 2.180(3)$ Å that leads to a distance of 3.10 Å between layers. The coordination polyhedron imposes a small rotation on the 2-carboxylate (dihedral angle 3(1)°) that may coordinate to the Na aristae-sharing chain that run along-*a*, thus preserving the pendant carboxylate observed in $Zn(2,4\text{-pydc})(H_2O)_4{\cdot}H_2O$ (**1**) and in $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$ (**3**).

A comparison between the 1:1 compounds **1** and **3**, also reveals marked differences that may be ascribed only to the electronic configuration of the metal ions. In $Zn(2,4\text{-pydc})(H_2O)_4{\cdot}H_2O$ the spherically symmetrical d^{10} configuration affords no ligand stabilization energy and Zn is situated in a distorted octahedron coordinating to five O and one N at varied distances and angles. In the centrosymmetric compound $[Ni(H_2O)_6][Ni(2,4\text{-pydc})_2(H_2O)_2]$, both Ni(II) ions show a more symmetric environment. Ni(1) and Ni(2) are found in the centre of an elongated octahedron with aqua ligands occupying the axial positions. The $2+2+2$ arrangement around Ni(1) was already found in other 2-pyridinecarboxylates such us $[Ni(3\text{-pyc})_2(H_2O)_2]{\cdot}2H_2O$ [18] and [Ni (H2,3-pydc)$_2$(H_2O)$_2$] [19]. These compounds illustrate the marked trend of the d^8 configuration to form symmetric planar compounds with two additional solvent molecules at larger distance. The tendency is strong and the 1:1 compound between 2,4-$pydc^{=}$ and Ni(II) markedly differs from the Zn(II) derivative. The former compound forms with two different Ni(II) centres where two 2,4-pydc and two H_2O molecules coordinate symmetrically to Ni(I) and six H_2O groups coordinate, also symmetrically to Ni(2).

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