

## A lithium complex of pyridine-2,6-dicarboxylic acid

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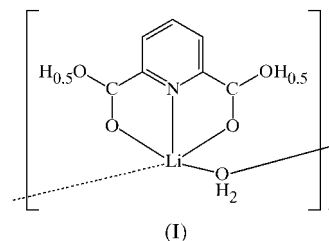
The crystal structure of *catena*-poly[[[6-carboxypyridine-2-carboxylato- $\kappa^3 O, N, O'$ ]lithium(I)]- $\mu$ -aqua- $\kappa^2 O:O$ ],  $[\text{Li}(\text{C}_7\text{H}_4\text{NO}_4)(\text{H}_2\text{O})]_n$ , contains the  $\text{Li}^+$  ion coordinated to two O atoms and the N atom of the 6-carboxypyridine-2-carboxylate ligand, and to two water O atoms, forming a pentavalent coordination geometry. The molecule resides on a mirror plane which contains the Li and N atoms, the *para*-CH unit, and the O atom of the coordinated water molecule. The O atom of the water molecule is coordinated to two Li atoms, forming an infinite polymeric chain.

### Comment

Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is a product of bacterial spores (Powell, 1953), accounting for approximately 5–15% of total spore dry weight (Church & Halvorson, 1959). The  $\text{Ca}^{2+}$  chelate of this organic compound is a major constituent of the dormant spore core (Murrell & Warth, 1965; Murrell, 1967), which is implicated as a factor in spore resistance properties and germination. Many crystal structures of pyridine-2,6-dicarboxylic acid chelated with divalent ions, such as  $\text{Ca}^{2+}$  (Strahs & Dickerson, 1968),  $\text{Ag}^{2+}$   $\{[\text{Ag}(\text{C}_7\text{H}_4\text{NO}_4)_2] \cdot \text{H}_2\text{O}$ ; Drew *et al.*, 1970),  $\text{Ti}^{2+}$  (Schwarzenbach, 1970),  $\text{Sr}^{2+}$  (Palmer *et al.*, 1972),  $\text{Ni}^{2+}$  (Quaglieri *et al.*, 1972),  $\text{Fe}^{2+}$  (Lainé, Gourdon & Launay, 1995; Lainé, Gourdon, Launay & Tuchagues, 1995),  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  (Okabe & Oya, 2000a), and  $\text{Mn}^{2+}$  (Okabe & Oya, 2000b), and with a monovalent metal ion,  $\text{Na}^+$  (Lainé, Gourdon & Launay, 1995), have been determined. In order to clarify the coordination mode of chelate compounds of pyridine-2,6-dicarboxylic acid with monovalent metal ions, we have analysed the crystal structure of the lithium derivative, (I).

In (I), the  $\text{Li}^+$  ion is coordinated by two carboxylate group O atoms and one N atom of the organic ligand. Around the central  $\text{Li}^+$  ion, five-membered rings (Li1/O1/C4/C1/N1 and Li1/O1'/C4'/C1'/N1) are formed [Li1—O1 2.152 (3) and Li1—N1 2.007 (10) Å, and C4—O1—Li1 116.9 (3), O1—C4—C1 113.0 (3) and C1—N1—Li1 120.2 (2)°]. This five-membered

ring formation is observed in all other crystal structures of metal complexes of pyridine-2,6-dicarboxylic acid.



In (I), two neighbouring  $\text{Li}^+$  ions are bridged by the O atom of a water molecule, to yield an infinite chain structure [O3—Li1 2.03 (1) and O3—Li1<sup>i</sup> 2.085 (10) Å; symmetry code: (i)  $x - 1, y, z$ ]. The crystal structure is stabilized by O3—H4 $\cdots$ O2<sup>ii</sup> hydrogen bonds between the water molecule and the carboxyl group of the organic ligand [symmetry code: (ii)  $-x, -y, 1 - z$ ], by O1—H3 $\cdots$ O1<sup>i</sup> hydrogen bonds between carboxyl groups of neighbouring ligand molecules and by a stacking interaction between the pyridine rings of the ligand molecules [N1 $\cdots$ N1<sup>iii</sup> 3.513 (5) Å; symmetry code:  $x + 1, y, z$ ]. Details of the hydrogen bonding are given in Table 2.

To date, many crystal structures of the chelate compounds of pyridine-2,6-dicarboxylic acid with metal ions have been analysed. In the crystal structures of chelate compounds with divalent ions, such as  $\text{Ag}^{2+}$  (Drew *et al.*, 1970),  $\text{Ni}^{2+}$  (Quaglieri *et al.*, 1972), and  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  (Okabe & Oya, 2000a), the ligand molecule is coordinated to a mononuclear metal ion and acts as a tridentate ligand, with the central metal ion bonded to two N atoms and four O atoms of two ligand molecules. The  $\text{Ca}^{2+}$  (Strahs & Dickerson, 1968),  $\text{Ti}^{2+}$  (Schwarzenbach, 1970),  $\text{Fe}^{2+}$  (Lainé, Gourdon & Launay, 1995; Lainé, Gourdon, Launay & Tuchagues, 1995) and  $\text{Mn}^{2+}$  (Okabe & Oya, 2000b) complexes are dinuclear, and the  $\text{Sr}^{2+}$  complex (Palmer *et al.*, 1972) is polynuclear. The complex with monovalent  $\text{Na}^+$  (Lainé, Gourdon & Launay, 1995) has a mononuclear structure. In our studies, the present  $\text{Li}^+$  complex and the  $\text{Cs}^+$  complex (Odoko *et al.*, 2001) are defined as

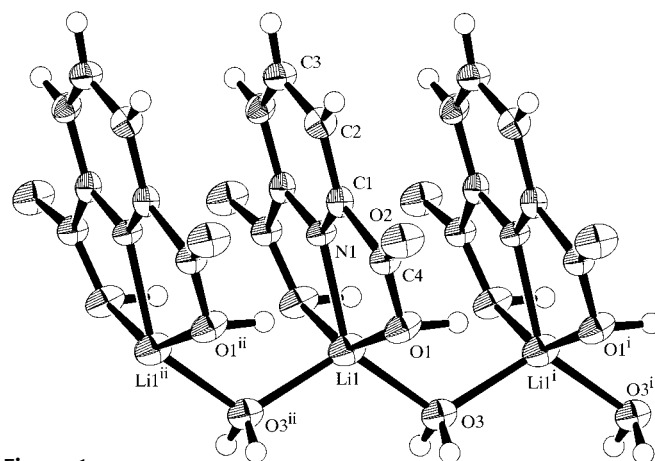


Figure 1

A view of the structure of (I) with the atomic numbering scheme. Displacement ellipsoids are at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atom H3 bonded to O1 has an occupancy of 0.5.

polynuclear. These results suggest that chelate compounds of pyridine-2,6-dicarboxylic acid with monovalent metal ions tend to form infinite polynuclear structures in the crystal, while divalent metal ion complexes tend to form mono- or dinuclear structures.

## Experimental

Crystals of (I) were obtained by slow evaporation of a 50% methanol solution of pyridine-2,6-dicarboxylic acid and lithium hydroxide in a 1:1 molar ratio at room temperature.

### Crystal data

[Li(C <sub>7</sub> H <sub>4</sub> NO <sub>4</sub> )(H <sub>2</sub> O)]	$D_x = 1.689 \text{ Mg m}^{-3}$
$M_r = 191.07$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 25 reflections
$a = 3.513 (2) \text{ \AA}$	$\theta = 13.5\text{--}14.8^\circ$
$b = 11.802 (2) \text{ \AA}$	$\mu = 0.14 \text{ mm}^{-1}$
$c = 9.191 (1) \text{ \AA}$	$T = 296.2 \text{ K}$
$\beta = 99.50 (2)^\circ$	Plate, colourless
$V = 375.8 (2) \text{ \AA}^3$	$0.4 \times 0.2 \times 0.1 \text{ mm}$
$Z = 2$	

### Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.024$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: $\psi$ scan	$h = 0 \rightarrow 4$
(North <i>et al.</i> , 1968)	$k = 0 \rightarrow 15$
$T_{\text{min}} = 0.966$ , $T_{\text{max}} = 0.986$	$l = -11 \rightarrow 11$
1056 measured reflections	3 standard reflections
910 independent reflections	every 150 reflections
598 reflections with $I > 2\sigma(I)$	intensity decay: <1%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1419P)^2 + 0.0837P]$
$R(F) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.235$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
910 reflections	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$
71 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters not refined	(Sheldrick, 1997)
	Extinction coefficient: 0.068

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O1—C4	1.290 (4)	N1—C1 <sup>ii</sup>	1.336 (4)
O1—Li1	2.152 (3)	N1—Li1	2.007 (10)
O2—C4	1.225 (4)	C1—C2	1.382 (5)
O3—Li1	2.03 (1)	C1—C4	1.511 (4)
O3—Li1 <sup>i</sup>	2.085 (10)	C2—C3	1.385 (4)
N1—C1	1.336 (4)		
C4—O1—Li1	116.9 (3)	O1—Li1—O1 <sup>ii</sup>	148.8 (4)
Li1—O3—Li1 <sup>i</sup>	117.3 (4)	O1—Li1—O3	97.1 (3)
C1—N1—Li1	120.2 (2)	O1—Li1—O3 <sup>iii</sup>	98.9 (3)
O1—C4—C1	113.0 (3)	O1—Li1—N1	75.4 (2)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x, \frac{1}{2} - y, z$ ; (iii)  $1 + x, y, z$ .

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H3 $\cdots$ O1 <sup>i</sup>	0.97	2.55	3.513 (2)	171
O3—H4 $\cdots$ O2 <sup>ii</sup>	0.83	1.98	2.775 (3)	160

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x, -y, 1 - z$ .

The H atoms were located from difference Fourier maps and were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *MITHRIL90* (Gilmore, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1090). Services for accessing these data are described at the back of the journal.

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