The Structure of Two Solid Zinc Dipicolinate Complexes

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Håkansson, K., Lindahl, M., Svensson, G. and Albertsson, J., 1993. The Structure of Two Solid Zinc Dipicolinate Complexes. – Acta Chem. Scand. 47: 449-455.

When equal amounts of dipicolinic (pyridine-2,6-dicarboxylic) acid and zinc sulfate were incubated at 277 K, two different zinc dipicolinate compounds of composition $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$ (1) and $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$ (2) were formed. An X-ray crystallographic investigation revealed that 1 comprises a solid dinuclear complex pentaaqua-μ-dipicolinatodipicolinatodizinc(II)–water(1/2) where two zinc ions are bridged by a carboxylate group. One zinc ion is coordinated by five water molecules and one carboxylate oxygen atom, and the other by four oxygen atoms and two nitrogen atoms from the two dipicolinate ligands. Compound 2 contains the mononuclear complex bis(hydrogendipicolinato)-zinc(II)–water(1/3), with the same zinc-dipicolinate coordination as in 1. In both 1 and 2 the coordination polyhedra are distorted octahedra with Zn–N = 2.003(4)–2.016(4) Å and Zn–O = 2.078(3)–2.349(3) Å. The compounds crystallize in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The cell parameters are: 1, $a = 8.382(2)$, $b = 27.408(6)$, $c = 9.709(3)$ Å and $\beta = 98.61(3)°$; 2, $a = 14.062(4)$, $b = 10.057(5)$, $c = 13.788(2)$ Å and $\beta = 116.55(3)°$.

Dipicolinic (2,6-pyridine dicarboxylic) acid is found in high concentrations in the protoplasts of dormant bacterial spores[1] and some fungi.[2] No explanation for this phenomenon has yet been found, nor has the physiological function of dipicolinate been revealed. Its importance for the heat stability of the spores has been debated.[3] Release of the bulk dipicolinate occurs as a late germination event, but a small amount has been observed to be released early.[4,5] When exogenously supplied, dipicolinate can act as a germinant itself.[6] In the bacterial spores dipicolinate appears to be present at least in part as a complex with calcium, the only protoplast metal ion present in excess over dipicolinate.[7] However, since a variety of metal ions can be chelated, and since bacterial spores contain several other metal ions, metal–dipicolinate complexes other than calcium dipicolinate might exist within the spores.

The dipicolinate ion is an effective tridentate chelating ligand forming stable complexes with most metal ions.[8] Many crystal structure determinations have elucidated various kinds of mono- and polynuclear complexes that are formed in the solid state.[9] The structure of calcium dipicolinate trihydrate, as determined by Strahs and Dickerson,[10] is of particular interest when discussing the biological function of the calcium dipicolinate complex. A close correlation has been found between zinc release and germination triggering of the bacterial spores.[11]

This motivated our structural study of the two different zinc dipicolinate compounds formed upon incubation of dipicolinate acid with zinc sulfate.

Experimental

Crystals of the two compounds were prepared by mixing hot aqueous solutions of zinc sulphate (25–50 mM) and dipicolinic acid (2,6-pyridine dicarboxylic acid, 25–50 mM) which were then left overnight at 277 K. The crystals of $Zn_2(DPA)_2 \cdot 7H_2O$ (1) grew as colourless bipyramids whereas $Zn(HDPA)_2 \cdot 3H_2O$ (2) formed colourless rods. The two phases were easily separated by hand under a microscope. The density of each compound was determined by flotation in a $CHCl_3/CHBr_3$ mixture. Crystal data and parameters pertinent to the intensity data collection and the structure determination and refinement of the two compounds are given in Table 1. The intensity data were measured on an Enraf-Nonius CAD-4 diffractometer at 292 K, using graphite-monochromated MoKα radiation ($\lambda = 0.710\,69$ Å). The unit cell dimensions were determined by least-squares fitting of the setting angles of 25 reflections in the ranges $7 < \theta < 14°$ (1) and $9 < \theta < 16°$ (2). The systematically absent reflections indicated space group $P2_1/c$ for both compounds.

Intensities were collected with $\omega/2\theta$ scans, $\Delta\omega = a + 0.50° \tan\theta$, $a = 0.80°$ (1) and 0.70° (2). The scan speed was automatically chosen to give $\sigma_c(I)/I \approx 0.03$ (σ_c from counting statistics) but with a limiting time of 90 s for 1 and 120 s for 2. Three intensity control reflections were measured every hour of X-ray exposure time for 1 and two

Table 1. Crystal data and the determination and refinement of the two zinc dipicolinate structures.

Compound	1	2
Formula	$Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$	$Zn(C_7H_4NO_4)_2 \cdot 3H_2O$
M_r	590.96	451.66
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a/Å$	8.382(2)	14.062(4)
$b/Å$	27.408(6)	10.057(5)
$c/Å$	9.709(3)	13.788(2)
$\beta/°$	98.61(3)	116.55(3)
$V/Å^3$	2205.4(7)	1744.3(2)
Z	4	4
$D_x/g\ cm^{-3}$	1.78	1.72
$D_m/g\ cm^{-3}$	1.77	1.73
$F(000)$	1192	920
μ/cm^{-1}	23.03	15.02
Crystal size/mm^3	$0.15 \times 0.30 \times 0.20$	$0.20 \times 15 \times 0.20$
Crystal colour	Colourless	Colourless
No. of faces	6	6
Grid for absorption correction	$8 \times 16 \times 12$	$10 \times 10 \times 10$
Transmission factor range	0.58–0.66	0.82–0.88
$h\ k\ l$ range: h	$-9 \rightarrow 0$	$0 \rightarrow 16$
k	$-32 \rightarrow 0$	$0 \rightarrow 11$
l	$-11 \rightarrow 11$	$-16 \rightarrow 16$
Measured reflections	4337	3447
Independent reflections	2784	3043
Observed reflections, $I > 3\sigma(I)$	2618	1839
R_{int}	0.059	0.033
Extinction coefficient	1.1×10^5	2.45×10^4
R, R_w	0.037, 0.046	0.037, 0.048
S	1.20	1.61
$(\Delta/\sigma)_{max}$	0.11	0.07
$\Delta\rho_{max}/\Delta\rho_{min}/e\ Å^{-3}$	0.62/−0.55	0.39/−0.53

control reflections every second hour for 2. The average decrease of their intensities was approximately 25 % for 1 and 3 % for 2 during the time of data collection. The intensity data were corrected for these decays and for the Lorentz, polarization and absorption effects, the latter by numerical integration.

In both structures the zinc atom position was located in Patterson maps and by direct methods (MULTAN80[12]). All non-hydrogen atoms, all hydrogen atoms in 1 and most hydrogen atoms in 2 were found in the subsequent $\Delta\rho$ maps. The missing atoms in 2 are the two acidic H atoms from the hydrogen dipicolinate ions and two water H atoms.

Refinements were carried out by a full-matrix least-squares minimization of $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2(F_o) + (kF_o)^2]^{-1}$; $k = 0.025$ for 1 and 0.020 for 2. Anisotropic displacement parameters were used for all non-hydrogen atoms. The hydrogen-atom parameters were refined over two cycles, with one common isotropic displacement parameter for hydrogen atoms attached to carbon and another for the water hydrogen atoms. Some extinction effects were discernible in 1, and an isotropic correction coefficient was included in the refinement of each structure. Two reflections from 1, (1 2 −1) and (2 0 −2), were so affected that they were excluded from the refinement. For both 1 and 2, all hydrogen-atom parameters and the extinction parameters were given

fixed values during the final stage of the least-squares refinement. The program system used in the crystallographic calculations has been described by Lundgren.[13] Atomic scattering and anomalous dispersion factors were taken from Ref. 14.

Results and discussion

The final atomic coordinates and equivalent isotropic displacement parameters for 1 and 2 are given in Tables 2 and 3, respectively.* Stereoviews of the two zinc complexes are shown in Fig. 1 and of the unit cell contents in Figs. 2 and 3. Selected bond distances and angles are given in Table 4. The compounds contain very similar bis(dipicolinato)zinc(II) (1) and bis(hydrogendipicolinato)zinc(II) (2) complexes, in 1 bridged via an outer carboxylate oxygen O9 to a pentaaquazinc(II) unit. Thus 1 contains a dinuclear complex; its systematic name should be pentaaqua-μ-pyridine-2,6-dicarboxylato-pyridine-2,6-dicarboxylatodizinc(II)–water(1/2), whereas the name of 2 is bis(hydrogenpyridine-2,6-dicarboxylato)-zinc(II)–water(1/3).

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* Lists of structure factors, anisotropic displacement parameters, H-atom positions, torsion angles, bond distances and angles involving H-atoms, hydrogen bond geometry and least-squares planes are available from one of the authors (K.H.).

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$ (1) with e.s.d.s in parentheses.

Atom[a]	x/a	y/b	z/c	U_{eq}[b]$/Å^2$
Zn1	−0.25978(6)	0.10154(2)	0.05492(5)	0.0291(2)
Zn2	0.25302(7)	0.11434(2)	0.15626(6)	0.0322(2)
N1	0.2161(4)	0.0432(1)	0.4690(3)	0.024(1)
C2	0.1056(5)	0.0294(2)	0.3614(5)	0.028(1)
C3	0.0853(5)	−0.0191(2)	0.3233(5)	0.032(1)
C4	0.1806(6)	−0.0534(2)	0.3991(5)	0.035(2)
C5	0.2912(5)	−0.0396(2)	0.5124(5)	0.030(1)
C6	0.3063(5)	0.0095(2)	0.5445(4)	0.024(1)
C7	0.0069(5)	0.0713(2)	0.2934(4)	0.028(1)
C8	0.4211(5)	0.0305(2)	0.6657(4)	0.028(1)
O9	−0.1087(4)	0.0598(1)	0.2005(3)	0.037(1)
O10	0.0454(4)	0.1138(1)	0.3362(4)	0.038(1)
O11	0.5030(4)	0.0022(1)	0.7466(3)	0.039(1)
O12	0.4227(4)	0.0769(1)	0.6743(3)	0.037(1)
N1′	0.2658(4)	0.1870(1)	0.5366(4)	0.028(1)
C2′	0.3623(5)	0.2132(2)	0.4680(5)	0.030(1)
C3′	0.3640(7)	0.2634(2)	0.4737(5)	0.042(2)
C4′	0.2606(7)	0.2868(2)	0.5518(6)	0.049(2)
C5′	0.1616(7)	0.2590(2)	0.6249(6)	0.045(2)
C6′	0.1700(6)	0.2093(2)	0.6157(4)	0.032(2)
C7′	0.4627(5)	0.1816(2)	0.3834(5)	0.031(2)
C8′	0.0790(6)	0.1729(2)	0.6956(5)	0.037(2)
O9′	0.5601(5)	0.2022(1)	0.3187(4)	0.050(1)
O10′	0.4349(4)	0.1364(1)	0.3841(3)	0.039(1)
O11′	−0.0119(5)	0.1895(2)	0.7732(4)	0.056(1)
O12′	0.1081(4)	0.1284(1)	0.6764(4)	0.043(1)
OW1	−0.2984(5)	0.0325(1)	−0.0310(4)	0.050(1)
OW2	−0.4142(4)	0.1316(1)	−0.1089(3)	0.040(1)
OW3	−0.0596(5)	0.1177(1)	−0.0388(4)	0.055(1)
OW4	−0.2134(4)	0.1640(1)	0.1760(4)	0.040(1)
OW5	−0.4771(4)	0.0889(1)	0.1527(3)	0.036(1)
OW6	0.2379(4)	0.4287(1)	0.4429(4)	0.049(1)
OW7	0.6575(5)	0.2934(2)	0.2383(5)	0.062(2)

[a] The two dipicolinate ions are denoted by primed and un-primed atomic symbols, respectively. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

The coordination geometries of the zinc ions are distorted octahedra, the distortion being somewhat less for the aqua part of the complex in 1 than for the dipicolinate part and the complex in 2. The dipicolinate ion is a rather rigid ligand, with $N \cdots O$ bites in the range 2.591(5)–2.626(6) Å in 1 and 2.610(6)–2.620(6) Å in 2. The corresponding N–Zn–O bite angles are 75.2(1)–77.2(1)° in 1 and 73.3(1)–79.4(1)° in 2. The ligand rigidity forces the coordinated carboxylate oxygen atoms to form flattened tetrahedra about the zinc ions instead of the planar squares of octahedra. The Zn–N bond distances, 2.003(4)–2.016(4) Å, are shorter than the Zn–O distances, 2.147(4)–2.275(3) Å in 1 and 2.078(3)–2.349(3) Å in 2. The Zn1 ion in 1 has five short bonds, to four water and the carboxylate oxygen atoms [average distance 2.077(9) Å] and one long bond to the fifth water oxygen atom [2.204(3) Å].

The geometries of the ligands in 1 and 2 are as expected. Bond distances and angles in the aromatic pyridine rings are in very good agreement with known values.[15] The rings are planar, with r.m.s. deviations 0.009 (unprimed atoms) and 0.010 (primed atoms) Å in 1. The corresponding values in 2 are 0.003 and 0.002 Å. The carboxylate

groups are to a varying but small degree twisted out of the ligand planes. The torsion angles N–C–C–O, where O is the oxygen atom coordinated to zinc, are in the range −3.8(6)–4.8(5)°. The carboxylate O10 and O12 atoms are coordinated to Zn. As a consequence the bonds C7–O10 and C8–O12 should be somewhat longer than C7–O9 and C8–O11.[16–18] This is the case for the primed molecule in 1 and unprimed C8–O11 but not for C7–O9. Since O9 is coordinated to Zn1 and O10 to Zn2 the two C7–O distances are equal. In 2, C7–O10 is longer than C7–O9, as expected, but the opposite is true for C8–O11 and C8–O12. The (not located) acid hydrogen atoms of the ligand ions in 2 may be bonded to O11, keeping C8–O11 long despite O12 being coordinated to Zn.[19, 20]

As can be seen from Fig. 2 and Table 4, hydrogen bonds involving the non-coordinated water molecules connect the dinuclear complexes in 1 into ribbons parallel to [001]. van der Waals interactions between the planar ligands of different complexes and further hydrogen bonding join these ribbons in three dimensions. The water molecules in 2 are only hydrogen-bonded to each other and the ligands. One of them, W3, is disordered, as can be seen from the displacement parameter for OW3 in Table

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$ (2) with e.s.d.s in parentheses.

Atom[a]	x/a	y/b	z/c	U_{eq}[b]$/Å^2$
Zn	0.24953(4)	0.00681(6)	0.73635(4)	0.0423(2)
N1	0.3941(3)	0.0863(3)	0.8234(3)	0.032(1)
C2	0.4558(3)	0.0967(4)	0.7732(3)	0.033(2)
C3	0.5531(4)	0.1587(5)	0.8215(4)	0.044(2)
C4	0.5872(4)	0.2111(5)	0.9260(4)	0.046(2)
C5	0.5229(4)	0.1986(5)	0.9777(4)	0.043(2)
C6	0.4267(3)	0.1353(4)	0.9238(3)	0.035(2)
C7	0.4069(4)	0.0359(4)	0.6604(3)	0.038(2)
C8	0.3467(4)	0.1134(4)	0.9668(4)	0.039(2)
O9	0.4603(3)	0.0335(3)	0.6093(3)	0.051(1)
O10	0.3126(2)	−0.0074(3)	0.6262(2)	0.046(1)
O11	0.3736(3)	0.1545(3)	1.0639(3)	0.054(2)
O12	0.2620(3)	0.0571(4)	0.9080(2)	0.048(1)
N1'	0.1042(3)	−0.0742(4)	0.6827(3)	0.033(1)
C2'	0.0215(3)	0.0065(5)	0.6317(3)	0.041(2)
C3'	−0.0825(4)	−0.0412(6)	0.5921(4)	0.052(2)
C4'	−0.0973(4)	−0.1725(7)	0.6069(4)	0.059(3)
C5'	−0.0112(4)	−0.2556(5)	0.6605(4)	0.049(2)
C6'	0.0901(3)	−0.2019(5)	0.6978(3)	0.038(2)
C7'	0.0511(5)	0.1491(5)	0.6228(4)	0.052(2)
C8'	0.1929(4)	−0.2750(5)	0.7583(3)	0.039(2)
O9'	−0.0220(3)	0.2271(4)	0.5732(3)	0.081(2)
O10'	0.1504(3)	0.1731(3)	0.6659(3)	0.052(2)
O11'	0.1830(3)	−0.3988(3)	0.7782(3)	0.056(2)
O12'	0.2769(2)	−0.2163(3)	0.7843(3)	0.048(1)
OW1	0.3470(3)	−0.5242(4)	0.8896(3)	0.058(2)
OW2	0.2480(4)	0.1107(4)	1.1374(4)	0.069(2)
OW3	0.1125(10)	−0.0515(9)	0.9963(7)	0.288(8)

[a] The two hydrogen dipicolinate ions are denoted by primed and un-primed atomic symbols, respectively. [b] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i \cdot a_j$.
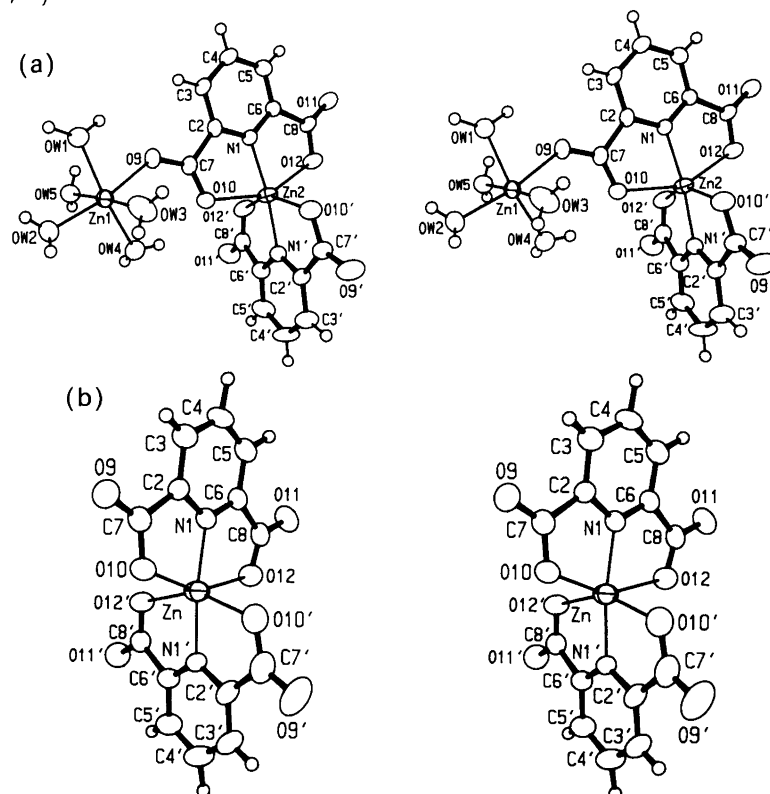

Fig. 1. (a) The dinuclear complex in compound 1, $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$, and (b) the mononuclear complex in 2, $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$. The acid hydrogen atoms are not located in 2. Thermal elipsoids are drawn with 50% probability.

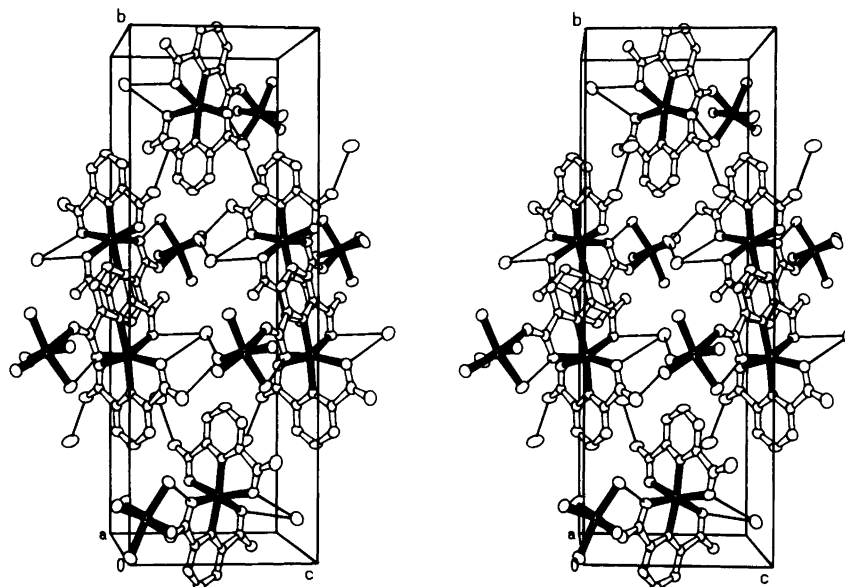*Fig. 2.* The unit cell content in compound 1, $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$. Thermal elipsoids as in Fig. 1. Thin lines indicate part of the hydrogen-bond system.
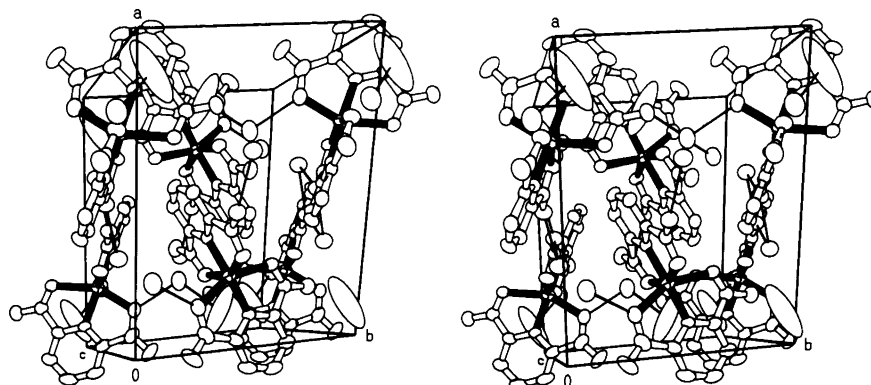

Fig. 3. The unit cell content in compound 2, $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$. Thermal elipsoids as in Fig. 1. Thin lines indicate part of the hydrogen-bond system.

Table 4. Selected bond distances (in Å) and angles (in °) for $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$ (1) and $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$ (2) with e.s.d.s in parentheses.

The zinc coordination

(1) $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$		(2) $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$	
Zn1–O9	2.092(3)		
Zn1–OW1	2.073(4)		
Zn1–OW2	2.066(3)		
Zn1–OW3	2.073(4)		
Zn1–OW4	2.081(3)		
Zn1–OW5	2.204(3)		
Zn2–N1	2.016(4)	Zn–N1	2.008(4)
Zn2–N1′	2.003(4)	Zn–N1′	2.009(4)
Zn2–O10	2.275(3)	Zn–O10	2.078(3)
Zn2–O10′	2.218(3)	Zn–O10′	2.115(4)
Zn2–O12	2.186(3)	Zn–O12	2.349(3)
Zn2–O12′	2.147(4)	Zn–O12′	2.322(4)
O9–Zn1–OW2	169.9(1)		
OW1–Zn1–OW4	169.4(1)		
OW3–Zn1–OW5	176.6(1)		
N1–Zn2–N1′	171.2(1)	N1–Zn–N1′	166.7(1)
O10–Zn2–O12	151.5(1)	O10–Zn–O12	152.5(1)
O10′–Zn2–O12′	152.0(1)	O10′–Zn–O12′	152.4(1)

Table 4. Continued

The dipicolinate ions

	(1) $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$		(2) $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$	
	Unprimed	Primed	Unprimed	Primed
N1–C2	1.343(5)	1.332(6)	1.334(5)	1.332(6)
N1–C6	1.340(5)	1.339(6)	1.342(5)	1.330(6)
C2–C3	1.384(7)	1.377(7)	1.375(6)	1.398(7)
C2–C7	1.507(7)	1.529(6)	1.519(6)	1.513(8)
C3–C4	1.376(7)	1.391(8)	1.403(7)	1.366(9)
C4–C5	1.382(6)	1.396(8)	1.384(7)	1.382(8)
C5–C6	1.383(6)	1.366(7)	1.374(6)	1.389(7)
C6–C8	1.518(6)	1.535(7)	1.504(6)	1.500(6)
C7–O9	1.261(5)	1.239(6)	1.238(6)	1.229(7)
C7–O10	1.263(6)	1.261(6)	1.270(6)	1.272(7)
C8–O11	1.236(6)	1.235(6)	1.286(5)	1.296(6)
C8–O12	1.274(6)	1.264(7)	1.238(6)	1.223(6)
C2–N1–C6	119.9(4)	120.2(4)	120.3(4)	121.0(4)
N1–C2–C3	121.4(4)	121.4(4)	121.5(4)	120.7(5)
N1–C2–C7	113.4(4)	112.9(4)	113.4(4)	114.5(4)
C3–C2–C7	125.2(4)	125.7(4)	125.1(4)	124.9(5)
C2–C3–C4	118.5(4)	118.7(5)	118.4(4)	118.5(5)
C3–C4–C5	120.3(4)	119.4(5)	119.5(4)	120.6(5)
C4–C5–C6	118.3(4)	118.1(5)	118.4(4)	118.1(5)
C5–C6–N1	121.5(4)	122.2(4)	121.8(4)	121.2(4)
N1–C6–C8	113.8(4)	112.3(4)	112.4(4)	112.7(4)
C5–C6–C8	124.7(4)	125.4(4)	125.7(4)	126.1(4)
C2–C7–O9	115.9(4)	118.2(4)	118.6(4)	117.2(5)
C2–C7–O10	117.5(4)	115.8(4)	116.0(4)	115.2(5)
O9–C7–O10	126.7(4)	125.9(4)	125.4(4)	127.5(5)
C6–C8–O11	118.8(4)	117.9(5)	116.1(4)	114.9(4)
C6–C8–O12	115.3(4)	115.6(4)	118.6(4)	119.4(4)
O11–C8–O12	125.8(4)	126.5(5)	125.3(4)	125.7(4)

Hydrogen bond distances

(1) $Zn_2(C_7H_3NO_4)_2 \cdot 7H_2O$

OW1 $\cdots$ O11 $(x-1, y, z-1)$	2.655(5)
OW1 $\cdots$ OW6 $(-x, y-\frac{1}{2}, \frac{1}{2}-z)$	2.992(5)
OW2 $\cdots$ OW7 $(x-1, \frac{1}{2}-y, z-\frac{1}{2})$	2.657(5)
OW2 $\cdots$ O12 $(x-1, y, z-1)$	2.774(5)
OW3 $\cdots$ OW6 $(x, \frac{1}{2}-y, z-\frac{1}{2})$	2.829(5)
OW3 $\cdots$ O11' $(x, y, z-1)$	2.753(6)
OW4 $\cdots$ O10 (x, y, z)	2.831(5)
OW4 $\cdots$ O9' $(x-1, y, z)$	2.720(5)
OW5 $\cdots$ O10' $(x-1, y, z)$	2.790(5)
OW5 $\cdots$ O11 $(-x, -y, 1-z)$	2.703(5)
OW6 $\cdots$ O12 $(x, \frac{1}{2}-y, z-\frac{1}{2})$	3.230(5)
OW6 $\cdots$ O12' $(x, \frac{1}{2}-y, z-\frac{1}{2})$	3.080(5)
OW6 $\cdots$ OW5 $(x-1, \frac{1}{2}-y, \frac{1}{2}+z)$	2.938(5)
OW7 $\cdots$ O11' $(1+x, \frac{1}{2}-y, z-\frac{1}{2})$	2.779(5)
OW7 $\cdots$ O9' $(x, y, z-1)$	2.777(6)

(2) $Zn(C_7H_4NO_4)_2 \cdot 3H_2O$

OW1 $\cdots$ O9 $(x, -y-\frac{1}{2}, \frac{1}{2}+z)$	2.723(5)
OW1 $\cdots$ O9 $(1-x, -y-\frac{1}{2}, 1\frac{1}{2}-z)$	2.766(5)
OW2 $\cdots$ OW3 (x, y, z)	2.601(10)
OW2 $\cdots$ O10' $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	2.692(5)

3. None of its hydrogen atoms nor the acid hydrogen atoms of the ligands could be located. Consequently we have not been able to elucidate the hydrogen-bond system fully.

Lindsay and Murell[21, 22] have suggested that calcium dipicolinate intercalation of protoplast DNA displaces intramolecular water, thus participating in the dehydration process and packaging of the DNA molecule. The structural similarity between calcium dipicolinate and zinc dipicolinate complexes indicates that the role of the metal is to neutralize the dipicolinate in an unspecific manner. Neutralization of the intercalator is required for its interaction with negatively charged DNA, but the availability of the different divalent metal ions rather than specific properties might determine the metal–dipicolinate composition in the bacterial spores.

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