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Copper(II) and zinc(II) complexes of pyridine-2,6-dicarboxylic acid

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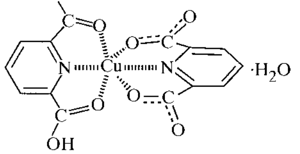
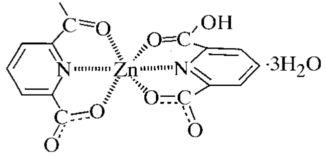
The title compounds, bis(pyridine-2,6-dicarboxylato-*N*,*O*,*O*′)copper(II) monohydrate, $[Cu(C_7H_4NO_4)_2]\cdot H_2O$, and bis(pyridine-2,6-dicarboxylato-*N*,*O*,*O*′)zinc(II) trihydrate, $[Zn(C_7H_4NO_4)_2]\cdot 3H_2O$, have distorted octahedral geometries about the metal centres. Both metal ions are bonded to four O atoms and two pyridyl-N atoms from the two terdentate ligand molecules, which are nearly perpendicular to each other. The copper(II) complex has twofold crystallographic symmetry and contains two different ligand molecules, one of which is neutral and another doubly ionized. In contrast, the zinc(II) complex contains two identical singly ionized ligand molecules. Both crystal structures are stabilized by O—H···O intermolecular hydrogen bonds between the complex and the water molecules.

Comment

Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is a compound produced by bacterial spores (Powell, 1953) which contain 5–15% of this compound on a dry weight basis (Church & Halvorson, 1959). It has been considered as the central component for the high heat resistance of bacterial spores based on the hypothesis that the metal chelates of pyridine-2,6-dicarboxylic acid with divalent metal ions within the spores construct a stabilizing structure analogous to bone substance in higher animals (Chung *et al.*, 1971). Many crystal structures of chelate compounds of pyridine-2,6-dicarboxylic acid with divalent ions such as Ca^{II} (Strahs & Dickerson, 1968), Ag^{II} (Drew *et al.*, 1969, 1970), Ti^{II} (Schwarzenbach, 1970), Sr^{II} (Palmer *et al.*, 1972), Fe^{II} (Lainé, Gourdon & Launay, 1995; Lainé, Gourdon, Launay & Tuchagues, 1995), and Ni^{II} and Cu^{II} (Quaglieri *et al.*, 1972) have been determined. In order to clarify the coordination modes of chelate compounds of pyridine-2,6-dicarboxylic acid with biologically important transition metal ions, we have analyzed the 1:2 complexes of transition metal ions Cu^{II} and Zn^{II} with pyridine-2,6-dicarboxylic acid as compounds (I) and (II), respectively.



(I)



(II)

In (I), the complex is located on a twofold axis of symmetry which passes through C3, N1, Cu1, N2 and C7 (Fig. 1 and Table 1) and contains two ligands with different degrees of deprotonation, one being neutral and the other dianionic. The Cu^{II} ion is bonded to the nitrogen [Cu1—N1 1.914 (4) Å] and two crystallographically equivalent negatively charged O atoms [Cu1—O2 2.019 (3) Å] of the dianionic ligand. It is also bonded, although less strongly, to the N atom [Cu1—N2 2.009 (4) Å] and two crystallographically equivalent ketonic O atoms [Cu1—O3 2.427 (3) Å] of the neutral ligand. In the 1:1 complex of Cu^{II} and pyridine-2,6-dicarboxylic acid (Quaglieri *et al.*, 1972), the Cu—N distance is 1.91 Å and that of Cu^{II}—O is 2.03 Å, which are comparable to the values for the doubly ionized ligand observed in this study. The bond angle C1—C4—O2 of 113.2 (3)° around the carboxylato-C atom of the dianionic ligand is significantly narrower than the corresponding angle C5—C8—O3 of 121.9 (4)° in the neutral ligand. These differences may depend on the electrostatic attractive force between the positively charged Cu^{II} ion and negatively charged O atoms of the dianionic ligand. The carboxylato groups of the dianionic ligand and the carboxyl groups of the neutral ligand lie almost in the plane of the corresponding pyridine ring, as indicated by the torsion angles O2—C4—C1—N1 [0.0 (5)°] and O3—C8—C5—N2 [−6.7 (6)°].

In contrast to (I), (II) contains two identical monoanionic ligands and has no crystallographically imposed symmetry (Fig. 2 and Table 3). The Zn^{II} ion is bonded to the pyridyl-N atoms [Zn1—N1 2.011 (2) and Zn1—N2 2.007 (2) Å], the two carboxylato-O atoms [Zn1—O4 2.070 (2) and Zn1—O8 2.115 (2) Å] and the two ketonic O atoms of the carboxyl groups [Zn1—O1 2.350 (2) and Zn1—O5 2.321 (2) Å]. The

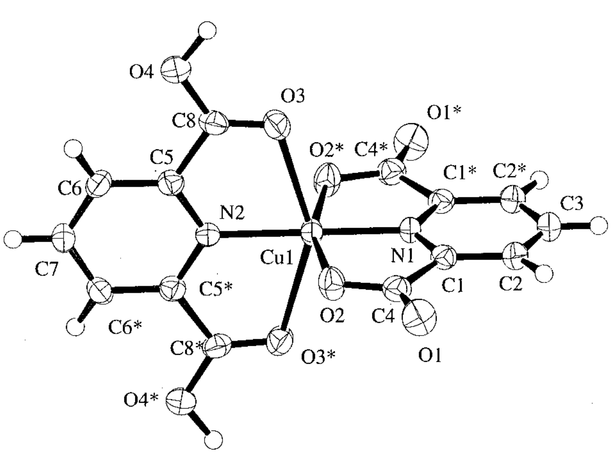


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. The symmetry code for each atom site with an asterisk is $(\frac{3}{2} - x, -y, z)$.

bond angles C5—C7—O4 [115.5 (2)°] and C12—C14—O8 [115.1 (2)°] around the carboxylato-C atoms are somewhat narrower than the corresponding angles around the carboxyl-C atoms C1—C6—O1 [119.0 (2)°] and C8—C13—O5 [119.5 (3)°]. These differences may also depend on the electrostatic attractive force between the positively charged Zn^{II} ion and negatively charged O atoms of the anionic carboxylato groups, as observed in the Cu^{II} complex. The carboxyl and carboxylato groups of the ligand molecules lie almost in the plane of the corresponding plane, as indicated by torsion angles N1—C5—C7—O3 of 175.1 (2), N1—C1—C6—O1 of 1.1 (3), N2—C8—C13—O5 of 3.3 (4) and N2—C12—C14—O7 of −177.8 (3)°.

The overall coordination modes about the Cu^{II} and Zn^{II} ions are similar with a distorted octahedral (*trans* meridional) geometry. Both metal ions are six-coordinate and are bonded similarly to the two N and four O atoms from the two terdentate ligand molecules, which are oriented nearly perpendicular to each other. However, the copper(II) complex contains two different ligands, one neutral and one dianionic, whereas the zinc(II) complex contains two identical monoanionic ligands. This different behaviour of the ligands may be a manifestation of the Jahn–Teller effect, which is exhibited by copper(II) with its d^9 electron configuration, but not by zinc(II) with d^{10}.

In all of the crystal structures of its 1:2 chelate complexes with transition metal ions, the ligand adopts an almost planar conformation, and acts as the terdentate ligand molecule in which the central metal ion is bonded to two N and four O atoms from two ligand molecules. The results of this study indicate not only that pyridine-2,6-dicarboxylic acid is a potential captor for transition metals in bacterial spores but also its likely coordination mode in such a role. This planar conformation is also observed in the free ligand (Takusagawa *et al.*, 1973).

In the crystal structures of both (I) and (II), molecules of the metal complex are connected by O—H···O-type hydrogen bonds to the uncoordinated water molecules (Tables 2 and 4). Stacking interactions between pyridine rings of the dianionic ligands are observed in the copper(II) complex, but not in the zinc(II) complex.

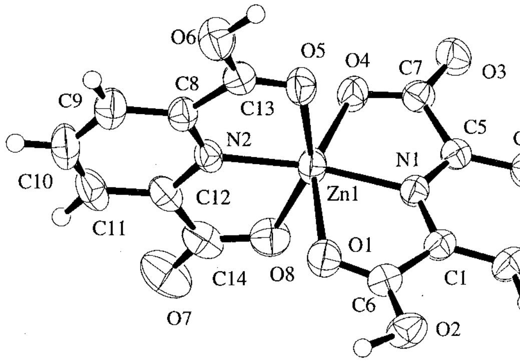


Figure 2
*ORTEP*II (Johnson, 1976) drawing of (II) with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

Experimental

Compound (I): the blue crystal used for analysis was obtained by slow evaporation from a solution in ethanol–water (1:1) of a mixture containing pyridine-2,6-dicarboxylic acid and copper(II) chloride dihydrate in a 4:1 molar ratio at room temperature. Compound (II): the colourless crystal used for analysis was obtained by the slow evaporation from a solution in ethanol–water (1:1) of a mixture containing pyridine-2,6-dicarboxylic acid and zinc(II) sulfate heptahydrate in a 4:1 molar ratio at room temperature.

Compound (I)

Crystal data

$[Cu(C_7H_4NO_4)_2]\cdot H_2O$
$M_r = 413.80$
Orthorhombic, *Pnna*
$a = 7.903$ (4) Å
$b = 11.068$ (4) Å
$c = 17.053$ (3) Å
$V = 1491$ (1) Å^3
$Z = 4$
$D_x = 1.843$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 14.1$–15.0°
$\mu = 1.523$ mm^{-1}
$T = 296$ K
Pillar, blue
0.40 × 0.10 × 0.10 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.784$, $T_{max} = 0.859$
1727 measured reflections
1727 independent reflections
1724 reflections with $I > 0$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 21$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.081$
$wR(F^2) = 0.129$
$S = 1.03$
1724 reflections
121 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.06$ e Å^{-3} (around the Cu atom)
$\Delta\rho_{min} = -0.75$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—O2	2.019 (3)	C4—O1	1.213 (5)
Cu1—O3	2.427 (3)	C4—O2	1.303 (4)
Cu1—N1	1.914 (4)	C8—O3	1.216 (5)
Cu1—N2	2.009 (4)	C8—O4	1.314 (5)
O2—Cu1—O3	95.3 (1)	C5—C6—C7	118.6 (4)
O2^i—Cu1—N1	80.10 (8)	C1—C4—O2	113.2 (3)
O3—Cu1—N2	74.50 (7)	C5—C8—O3	121.9 (4)
O3^i—Cu1—N1	105.50 (7)		

Symmetry code: (i) $\frac{3}{2} - x, -y, z$.

Table 2
Hydrogen-bonding and short contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H5···O5^i	1.03	1.61	2.621 (4)	168
O5···O2			2.638 (4)	

Symmetry code: (i) $1 + x, y, z$.

Compound (II)

Crystal data

$[Zn(C_7H_4NO_4)_2]\cdot 3H_2O$
$M_r = 451.65$
Monoclinic, $P2_1/a$
$a = 13.765$ (2) Å
$b = 10.052$ (2) Å
$c = 14.060$ (2) Å
$\beta = 116.554$ (8)°
$V = 1740.3$ (4) Å^3
$Z = 4$

$D_x = 1.724$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 14.8$–$15.0°$
$\mu = 1.477$ mm^{-1}
$T = 296$ K
Pillar, colourless
$0.50 \times 0.15 \times 0.15$ mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.755$, $T_{\rm max} = 0.801$
4392 measured reflections
3991 independent reflections
3991 reflections with $I > 0$

$R_{\rm int} = 0.017$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = -18 \rightarrow 16$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.058$
$wR(F^2) = 0.114$
$S = 1.36$
3991 reflections
253 parameters

H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.81$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.63$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—O1	2.350 (2)	C6—O2	1.287 (3)
Zn1—O4	2.070 (2)	C7—O3	1.235 (3)
Zn1—O5	2.321 (2)	C7—O4	1.264 (3)
Zn1—O8	2.115 (2)	C13—O5	1.224 (3)
Zn1—N1	2.011 (2)	C13—O6	1.286 (3)
Zn1—N2	2.007 (2)	C14—O7	1.223 (4)
C6—O1	1.230 (3)	C14—O8	1.227 (4)
O1—Zn1—O4	152.33 (8)	O5—Zn1—N1	102.60 (8)
O1—Zn1—O5	89.54 (8)	O5—Zn1—N2	74.01 (8)
O1—Zn1—O8	91.69 (8)	O8—Zn1—N1	104.18 (8)
O1—Zn1—N1	73.21 (8)	O8—Zn1—N2	78.36 (9)
O1—Zn1—N2	93.44 (8)	N1—Zn1—N2	166.39 (8)
O4—Zn1—O5	94.18 (8)	C1—C6—O1	119.0 (2)
O4—Zn1—O8	97.39 (8)	C5—C7—O4	115.5 (2)
O4—Zn1—N1	79.22 (8)	C8—C13—O5	119.5 (3)
O4—Zn1—N2	113.95 (8)	C12—C14—O8	115.1 (2)
O5—Zn1—O8	152.37 (8)		

The H atoms of the carboxyl groups in (I) and (II) were located from difference Fourier maps. Other H atoms were initially located from difference Fourier maps, removed and then placed in calculated positions. The two H atoms bonded to O5 of the water molecule in (I) are not found in the Fourier maps, but are accounted for in the formula sum and formula weight calculations.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H4$\cdots$O10	1.08	1.40	2.462 (4)	166
O6—H8$\cdots$O9$^{\rm i}$	1.03	1.45	2.483 (2)	174
O9—H9$\cdots$O3$^{\rm ii}$	0.87	1.93	2.762 (3)	160
O9—H10$\cdots$O3$^{\rm iii}$	0.92	1.80	2.719 (3)	175
O10—H11$\cdots$O8$^{\rm iii}$	1.02	1.69	2.679 (3)	164
O10—H12$\cdots$O11$^{\rm iv}$	0.90	1.84	2.623 (6)	145
O11—H13$\cdots$O11$^{\rm iv}$	0.93	2.39	3.28 (2)	159

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, 2-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iv) $2-x, -y, 1-z$.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992*b*); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989) and *DIRDIF*94 (Beurskens *et al.*, 1992); program(s) used to refine structure: *TEXSAN/LS* (Molecular Structure Corporation, 1992*b*); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1356). Services for accessing these data are described at the back of the journal.

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