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Poly[[[diaquazinc(II)]-bis(μ_2-3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olato-κ^2N^3:$N^{3'}$)] dihydrate]

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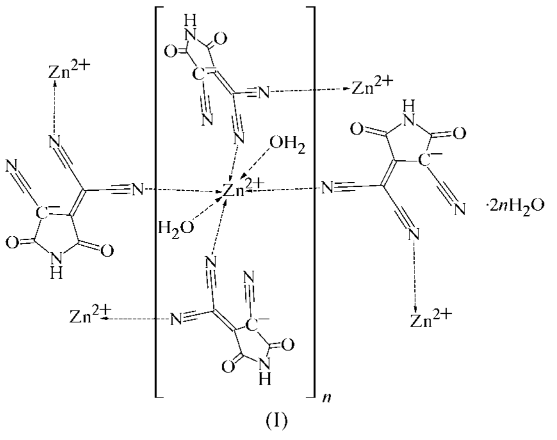
The coordination of the 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate anion to Zn^{II}, the apical sites of which are occupied by two water molecules, results in the formation of two-dimensional layers of the title coordination polymer, $\{[Zn(C_8HN_4O_2)_2(H_2O)_2]\cdot 2H_2O\}_n$, in which the Zn^{II} cations lie on inversion centres in space group *C*2/*c*, with water ligands in the apical sites of octahedral geometry. Hydrogen bonds between coordinated and lattice water molecules, and π–π stacking interactions between the anions link adjacent layers into a continuous framework.

Comment

We have recently postulated that the new organic anion 3-cyano-4-dicyanomethylene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate could be involved in different types of anion–cation interaction (Tafeenko, Peschar *et al.*, 2004). Specifically, we proposed that this anion could be involved in π–π stacking interactions and that it could form coordination compounds. Subsequently, π–π stacking interactions have been detected not only between cations and this anion, but also between pairs of anions (Tafeenko *et al.*, 2003, 2005; Tafeenko, Nikolaev *et al.*, 2004). We report here the first example of a metal coordination compound, the title compound, (I), where the anion coordinates to Zn^{II} (Fig. 1).



(I)

The geometry of the anion in (I) (Table 1) is essentially identical to that found in other salts (Tafeenko *et al.*, 2003, 2005; Tafeenko, Peschar *et al.*, 2004; Tafeenko, Nikolaev *et al.*, 2004), although some minor differences are apparent. The C6—C7 and C6—C8 bonds are shorter than the corresponding bonds found in salts with different cations, namely potassium (Tafeenko *et al.*, 2003), *N*,*N*-dimethylanilinium (Tafeenko, Peschar *et al.*, 2004), *N*-methylpyridinium (Tafeenko, Nikolaev *et al.*, 2004) and ammonium (Tafeenko *et*

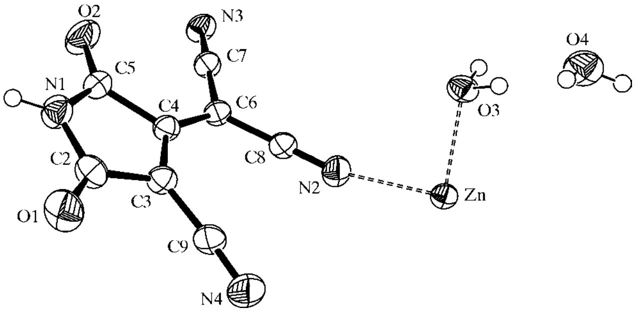


Figure 1
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

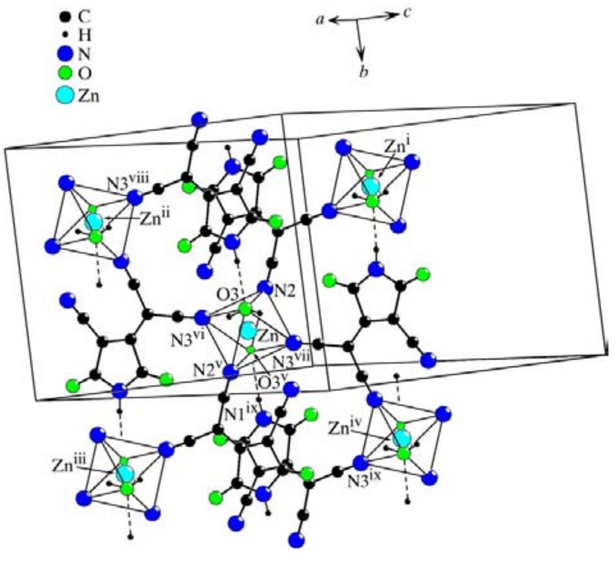


Figure 2
Part of the crystal structure of (I), showing how the cations and anions are arranged to form a layer. The Zn atom at (x, y, z) and those with symmetry codes (i)–(iv) lie in the same plane. Infinite $[Zn(C_8HN_4O_2)_2(H_2O)_2]_n$ chains are formed along the b axis *via* O3···H1—N1 hydrogen bonds. Adjacent chains are connected by coordination of an N3 atom from one chain to a Zn atom of another chain. In the layer, anions of adjacent chains form dimers *via* π–π interactions, *e.g.* the anion at (x, y, z) and its coordinated Zn^{II} cation form a dimer with the anion at symmetry position (viii), which is related to cation Zn^{ii}. The Zn···Zn^{i,ii,iii,iv} distances are equal at 8.185 (1) Å. [Symmetry codes: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, \frac{3}{2} - y, -z$; (vi) $x, 1 - y, -\frac{1}{2} + z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (ix) $x, 1 + y, z$.]

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al., 2005). The C9—C4—C6—C7 torsion angle found here has the largest value in this series. This may be compared with the value of 7.5 (1)° in the potassium salt, while for all other salts this value is substantially smaller.

The Zn^{II} cation of (I) is located on an inversion centre. The coordination sphere consists of water O atoms [O3 and O3^{v}; symmetry code: (v) $\frac{1}{2}-x, \frac{3}{2}-y, -z$] and cyano N atoms [N2, N2^{v}, N3^{vi}, N3^{vii}; symmetry codes: (vi) $x, 1-y, -\frac{1}{2}+z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$] of four anions (Fig. 2). The Zn—N3 bond is shorter than Zn—O3 and Zn—N2 (Table 1). In the coordination octahedron, the basal angles O—Zn—N and N—Zn—N are in the range 87.80 (7)–92.20 (7)°, so that the octahedral geometry is nearly ideal. Each anion links two Zn^{II} centres by means of the dicyanomethylene units. Each Zn^{II} cation is connected to four others by four different anions to form two-dimensional layers of the $[Zn(C_8H_1N_4O_2)_2(H_2O)_2]_n$ coordination polymer. Two additional solvent water molecules complete the composition.

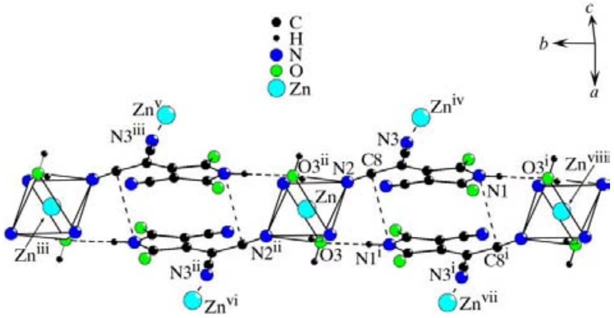

Figure 3
Part of the chain, showing how the building blocks [each consisting of a Zn^{II} cation, two water molecules and two anions, *e.g.* with symmetry codes (x, y, z) and (ii)] interplay through the complementary hydrogen-bonding and π–π interactions. The hydrogen-bond parameters are listed in Table 2. The shortest distance between anions from adjacent blocks in the chain is N1$\cdots$C8^{i} = 3.265 Å. Adjacent chains are linked by a coordination bond from N3 to Zn, thus forming a layer. [Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (ii) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (iii) $x, 1+y, z$; (iv) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$; (vii) $\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (viii) $x, -1+y, z$.]

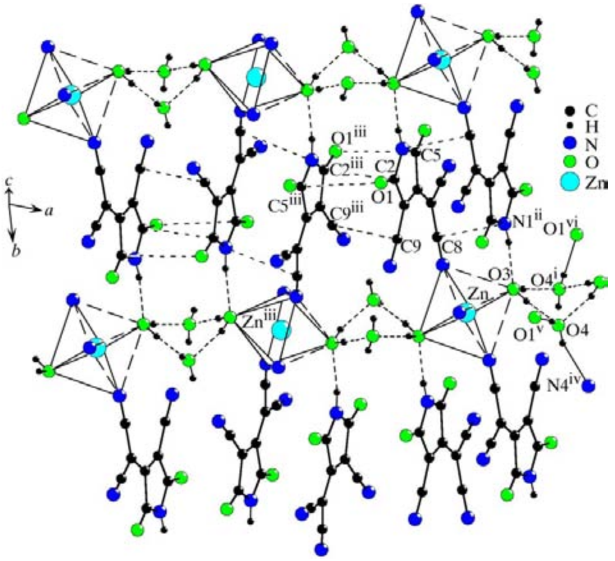

Figure 4
The anions of adjacent layers [*e.g.* an anion at (x, y, z) and an anion with symmetry code (iii)] are connected by π–π interactions to form stacks running normal to the *bc* plane. Hydrogen bonds between the apical (O3) and hydrate (O4) water molecules enhance the interaction. Some distances between atoms of adjacent layers are C9$\cdots$C9^{iii} = 3.322 (4) Å, O1$\cdots$C5^{iii} = 3.272 (3) Å, C2$\cdots$C2^{iii} = 3.266 (3) Å and C5$\cdots$O1^{iii} = 3.272 (3) Å. The hydrate molecules form hydrogen bonds with atoms O1 and N4 of the anions. The parameters of the hydrogen bonds are listed in Table 2. The distance between Zn atoms in the direction normal to the *bc* plane (*e.g.* Zn$\cdots$Zn^{iii}) is the shortest [7.445 (1) Å]. [Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $-x, y, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.]

The two-dimensional layer formation is shown in detail in Figs. 2 and 3, and the interactions betweeen these layers are shown in Fig. 4. The building block of the polymer consists of a Zn^{II} cation, two water molecules and two anions (Fig. 3). It resembles a slightly deformed letter Z. An arrangement of these building blocks in a $\cdots$ZZZ$\cdots$ fashion can, most probably, occur in coordination compounds containing transition metals. The synthesis and structure investigation of such compounds would be of interest, given that coordination polymers containing cyano-based anions have exhibited long-range magnetic ordering (Kurmoo & Kepert, 1998; Batten *et al.*, 1998).

Experimental

The synthesis of the title salt was carried out by Dr O. V. Kaukova, Department of Chemistry, Chuvash State University, Russia, and was obtained by mixing zinc iodide with 2,2,3,3-tetracyanocyclopropanecarboxylic acid in the molar ratio 1:2. The reaction was carried out in water–propan-2-ol (1:1 *v*/*v*) at room temperature. A yellow powder was extracted from the reaction mixture by filtration and drying. Yellow crystals of (I) were obtained after slow evaporation of a solution in acetonitrile over a period of 7 d.

Crystal data

$[Zn(C_8HN_4O_2)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 507.69$
Monoclinic, $C2/c$
$a = 19.0297\ (17)$ Å
$b = 11.0300\ (19)$ Å
$c = 12.0952\ (19)$ Å
$\beta = 128.519\ (9)^\circ$
$V = 1986.3\ (6)$ Å^3
$Z = 4$

$D_x = 1.698$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 29$–46°
$\mu = 2.33$ mm^{-1}
$T = 290\ (2)$ K
Prism, yellow
0.10 × 0.06 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.861$, $T_{max} = 0.920$
3976 measured reflections
1985 independent reflections
1821 reflections with $I > 2\sigma(I)$

$R_{int} = 0.09$
$\theta_{max} = 72.9^\circ$
$h = -23 \rightarrow 23$
$k = -11 \rightarrow 13$
$l = -12 \rightarrow 14$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.100$
$S = 1.07$
1985 reflections
171 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.4794P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -1.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N3^{i}	2.0830 (17)	N4—C9	1.146 (3)
Zn—O3	2.1344 (14)	C2—C3	1.466 (3)
Zn—N2	2.1406 (19)	C3—C4	1.381 (3)
O1—C2	1.216 (3)	C3—C9	1.417 (3)
O2—C5	1.205 (3)	C4—C6	1.387 (3)
N1—C5	1.367 (3)	C4—C5	1.527 (3)
N1—C2	1.389 (3)	C6—C7	1.415 (3)
N2—C8	1.145 (3)	C6—C8	1.415 (3)
N3—C7	1.146 (3)		
N3^{i}—Zn—O3	89.60 (7)	O3—Zn—N2	89.95 (7)
N3^{i}—Zn—N2	92.20 (7)		

Symmetry code: (i) $x, -y+1, z-\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{iv}	0.90 (4)	2.06 (4)	2.962 (3)	172 (4)
O3—H2···O4	0.92 (4)	1.84 (4)	2.762 (2)	172 (4)
O3—H3···O4^{v}	0.78 (3)	1.99 (3)	2.748 (2)	163 (3)
O4—H4···O1^{vi}	0.82 (2)	1.97 (2)	2.782 (3)	172 (4)
O4—H5···N4^{vii}	0.84 (2)	2.21 (2)	3.017 (3)	161 (4)

Symmetry codes: (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (v) $-x+1, y, -z+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, y+\frac{1}{2}, -z-\frac{1}{2}$; (vii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

The positions of the H atoms were determined from a Fourier difference map and their coordinates were refined freely with isotropic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1389). Services for accessing these data are described at the back of the journal.

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