Bis[6-amino-3-methyl-5-nitroso-pyrimidine-2,4(1H,3H)-dionato]-diaquazinc(II) dihydrate, redetermined at 120 K: a three-dimensional hydrogen-bonded framework

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The title compound, whose structure has been redetermined at 120 K, contains almost centrosymmetric *trans*-[Zn(C$_5$H$_5$N$_4$O$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O units, together with two uncoordinated water molecules. An extensive series of O—H···O, O—H···N and N—H···O hydrogen bonds gives rise to a three-dimensional framework structure.

Comment

We have recently reported detailed analyses of the supramolecular structures of neutral 6-amino-3-methyl-5-nitroso-pyrimidine-2,4(1H,3H)-dione, (1) (Godino Salido *et al.*, 2003), as well as of those of the hydrated sodium, strontium and barium complexes of the 6-amino-3-methyl-5-nitroso-pyrimidine-2,4(1H,3H)-dionate anion, (2) (Cuesta *et al.*, 2001; Low *et al.*, 2003; López Garzón *et al.*, 2003). The structure of the corresponding hydrated zinc complex bis[6-amino-3-methyl-5-nitrosopyrimidine-2,4(1H,3H)-dionato]diaqua-zinc(II) dihydrate, (I), was determined some years ago (Moreno *et al.*, 1986) from data collected at ambient temperature, but no analysis or description of the supramolecular structure was given; accordingly, we have now re-investigated this complex using data collected at 120 (2) K, and present here a detailed description of the hydrogen-bonded supramolecular structure. The unit-cell dimensions and atomic coordinates show clearly that the same phase is present at both 120 and 293 K.

The molecular structures at 120 and 298 K are essentially the same, with *trans* diaxial water molecules coordinated to zinc in an octahedral complex whose structure, although close

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to being centrosymmetric (Fig. 1), shows significant deviation from centrosymmetry (Table 1); each of the anionic ligands contains the usual intramolecular N—H···O hydrogen bond with the nitroso O atoms as acceptor. The bond distances in the two anions are very similar (Table 1), and there are some unexpected values; firstly, the bonds Nn1—Cn2 (n = 1 or 2) are longer than Nn1—Cn6; secondly, the bonds Cn4—Cn5 and Cn5—Cn6 are very similar in length; finally, the bonds Cn4—On4 are significantly longer than Cn2—On2. These observations taken together indicate the importance of form (2a) as a contributor to the overall molecular–electronic structure, alongside form (2).

(I)
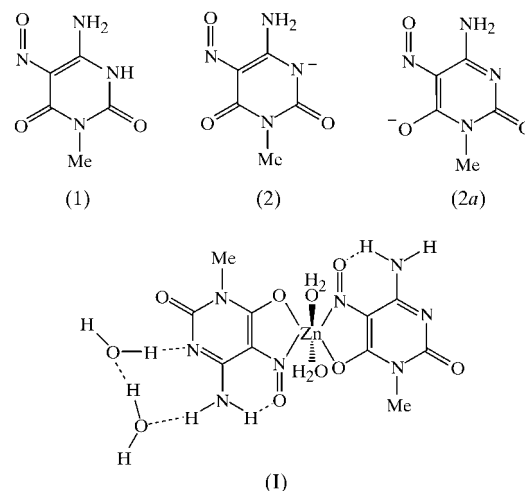
Within the asymmetric unit selected here, atom N16 acts as a hydrogen-bond donor to water atom O3, which itself acts as a donor *via* H3A to water atom O4, and this in turn acts as a donor *via* H4B to N11, so forming an $R_3^3(8)$ motif (Bernstein *et al.*, 1995) (Fig. 1). There are thus six O—H bonds and one N—H bond not engaged in hydrogen bonding within the asymmetric unit (Table 2); these are thus all available to link the three-component aggregates, so forming a three-dimensional framework whose construction can be readily understood by use of the substructure approach (Gregson *et al.*, 2000).
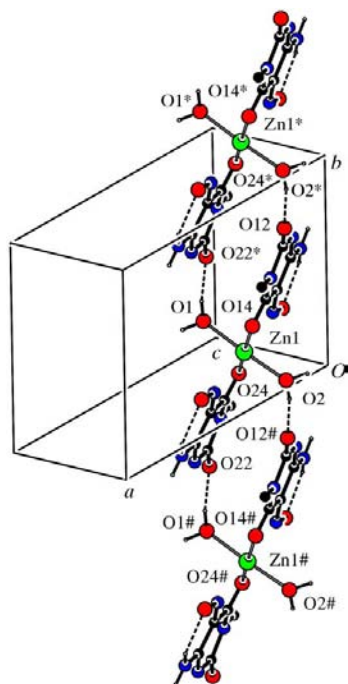
Coordinated water atom O1 in the aggregate at (x, y, z) acts as a hydrogen-bond donor, *via* H1A, to amide atom O22 in the aggregate at (x, 1 + y, z), while O2 at (x, y, z) acts as a donor,
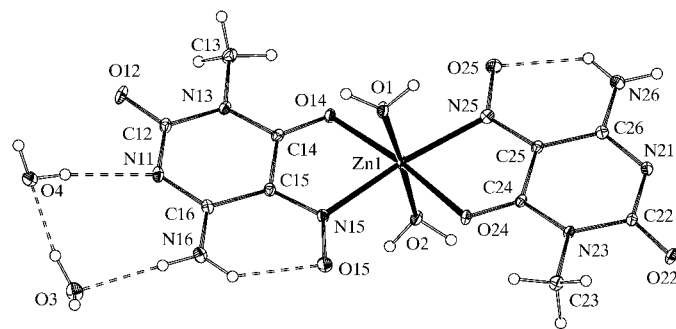
Figure 1
The independent components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
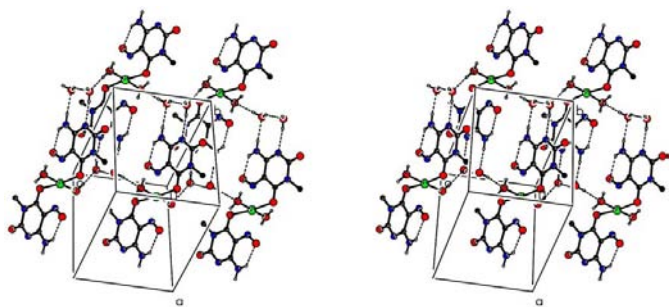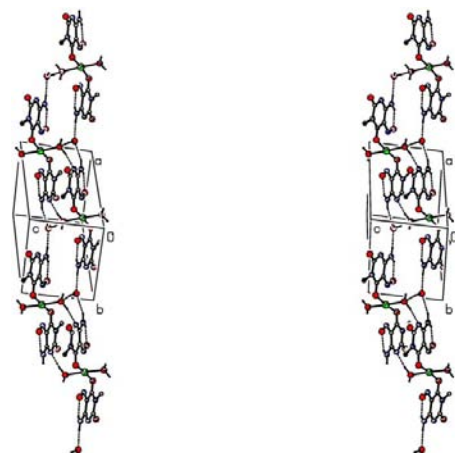
metal-organic compounds

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of spiro-fused rings along [010]. For the sake of clarity, H atoms bonded to C atoms have been omitted, as have the non-coordinated water molecules. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, -1 + y, z)$, respectively.

via H2A, to amide atom O12 at $(x, -1 + y, z)$. The combination of these two hydrogen bonds generates a chain of spiro-fused $R_2^2(16)$ rings running parallel to the [010] direction (Fig. 2). This [010] chain is reinforced by the action of water atom O4 at (x, y, z), which acts as a hydrogen-bond donor, *via* H4A, in a weak but nearly planar three-centre $O-H\cdots(O)_2$ system in which the acceptors are atoms O15 and O24 in the aggregate at $(x, 1 + y, z)$.

Water atom O1 at (x, y, z) also acts as a hydrogen-bond donor, this time *via* H1B, to ring atom N21 in the aggregate at $(1 - x, y, 1 - z)$, so producing an $R_2^2(16)$ ring centred at $(\frac{1}{2}, 0, \frac{1}{2})$; O2 at (x, y, z) likewise acts as a donor, *via* H2B, to water atom O4 at $(-x, 1 - y, -z)$, producing an $R_4^4(20)$ ring centred at $(0, \frac{1}{2}, 0)$; and O3 at (x, y, z) acts as a donor, *via* H3B, to atom

Figure 3
Stereoview of part of the crystal structure of (I), showing the formation of a [001] chain of fused $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Figure 4
Stereoview of part of the crystal structure of (I), showing the formation of a $[1\bar{1}0]$ chain of fused $R_2^2(16)$ and $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms and to water atom O4 have been omitted.
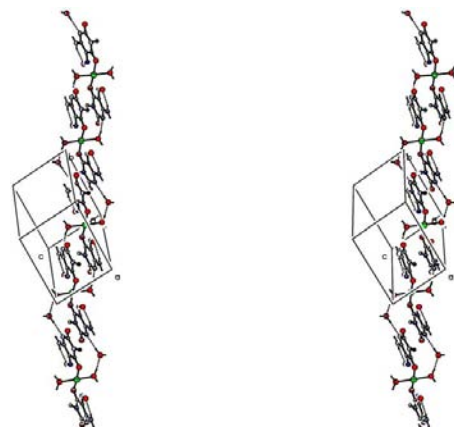
Figure 5
Stereoview of part of the crystal structure of (I), showing the formation of a $[1\bar{1}1]$ chain of fused $R_2^2(16)$ and $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms and to water atom O3 have been omitted.

O1 at $(-x, 1 - y, 1 - z)$, producing a third ring, this time of the $R_4^4(20)$ type centred at $(0, \frac{1}{2}, \frac{1}{2})$. The combination of the $(0, \frac{1}{2}, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$ rings produces a chain of rings along [001] (Fig. 3); the combination of the $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$ rings produces a chain of rings along $[1\bar{1}0]$ (Fig. 4), and the combination of the $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$ rings produces a chain of rings along $[1\bar{1}1]$ (Fig. 5). The combination of the [001], $[1\bar{1}0]$ and $[1\bar{1}1]$ chains generates a (110) sheet, and the combination of (110) sheets with [010] chains (Fig. 2) generates a single three-dimensional framework.

Experimental

Compound (I) was prepared by addition of a threefold molar excess of zinc chloride to a solution of the corresponding potassium salt in methanol/water (9/1, *v/v*). Slow evaporation of the resulting solution gave orange crystals of analytically pure (I). Analysis found: C 25.5, H 4.1, N 23.6%; $C_{10}H_{18}N_8O_{10}Zn$ requires: C 25.2, H 3.8, N 23.6%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample.

Crystal data

[Zn(C$_5$H$_5$N$_4$O$_3$)$_2$(H$_2$O)$_2$]·2H$_2$O
$M_r = 475.69$
Triclinic, $P\bar{1}$
$a = 11.3625$ (2) Å
$b = 9.5848$ (2) Å
$c = 8.0433$ (2) Å
$\alpha = 102.2410$ (8)°
$\beta = 94.2412$ (11)°
$\gamma = 97.7735$ (11)°
$V = 843.41$ (3) Å^3

$Z = 2$
$D_x = 1.873$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3873
  reflections
$\theta = 3.0\text{–}27.5°$
$\mu = 1.53$ mm^{-1}
$T = 120$ (2) K
Block, orange
$0.40 \times 0.20 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan
  (*DENZO–SMN*; Otwinowski &
  Minor, 1997)
  $T_{min} = 0.579$, $T_{max} = 0.803$
15 390 measured reflections

3873 independent reflections
3652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.102$
$S = 1.21$
3873 reflections
264 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2$
  $+ 0.5527P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.82$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	2.1428 (16)	C15—N15	1.327 (3)
Zn1—O14	2.0913 (15)	N15—O15	1.279 (2)
Zn1—N15	2.1228 (18)	C16—N16	1.320 (3)
Zn1—O2	2.1200 (15)	N21—C22	1.361 (3)
Zn1—O24	2.1442 (15)	C22—N23	1.418 (3)
Zn1—N25	2.1205 (19)	N23—C24	1.358 (3)
N11—C12	1.362 (3)	C26—N21	1.340 (3)
C12—N13	1.414 (3)	C22—O22	1.229 (3)
N13—C14	1.354 (3)	N23—C23	1.468 (3)
C16—N11	1.337 (3)	C24—O24	1.254 (3)
C12—O12	1.224 (3)	C25—N25	1.348 (3)
N13—C13	1.477 (3)	N25—O25	1.264 (2)
C14—O14	1.248 (3)	C26—N26	1.320 (3)
O14—Zn1—O24	172.82 (5)	O1—Zn1—O2	176.78 (6)
N15—Zn1—N25	171.51 (7)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N16—H16A⋯O3	0.88	2.03	2.906 (3)	175
N16—H16B⋯O15	0.88	2.04	2.694 (3)	131
N26—H26A⋯O3^i	0.88	2.25	3.063 (3)	154
N26—H26B⋯O25	0.88	2.05	2.696 (3)	130
N26—H26B⋯O2^{ii}	0.88	2.44	3.034 (3)	125
O1—H1A⋯O22^{iii}	0.88	1.87	2.728 (2)	164
O1—H1B⋯N21^{iv}	0.94	1.84	2.763 (2)	166
O2—H2A⋯O12^v	0.89	1.80	2.670 (2)	168
O2—H2B⋯O4^{vi}	0.91	1.85	2.754 (2)	169
O3—H3A⋯O4	0.88	2.01	2.795 (3)	147
O3—H3B⋯O1^{vii}	0.81	2.23	2.946 (2)	148
O4—H4A⋯O24^{iii}	0.84	2.40	3.091 (2)	140
O4—H4A⋯O15^{iii}	0.84	2.57	3.250 (2)	138
O4—H4B⋯N11	0.82	2.10	2.919 (2)	172

Symmetry codes: (i) $1 + x, y - 1, z$; (ii) $1 - x, -y, -z$; (iii) $x, 1 + y, z$; (iv) $1 - x, -y, 1 - z$; (v) $x, y - 1, z$; (vi) $-x, 1 - y, -z$; (vii) $-x, 1 - y, 1 - z$.

Crystals of (I) are triclinic and space group $P\bar{1}$ was selected and confirmed by the successful structure solution and refinement. It was clear from an early stage that the atomic coordinates were essentially the same as those found in the ambient-temperature study (Moreno *et al.*, 1986). To facilitate comparison with that study, we have retained the same non-conventional cell setting, although we have used the same atom-labelling scheme as used in our previous studies; in addition, we have used positions for the two non-coordinated water molecules which differ from those adopted earlier. H atoms bonded to C and N atoms were treated as riding atoms, with C—H distances of 0.98 Å and N—H distances of 0.88 Å; the H atoms bonded to O atoms were all located from difference maps and allowed to ride at the O—H distances deduced from the maps, *viz.* 0.81–0.94 Å. The principal differences between the refinement reported here and that reported previously concern the weighting scheme, the convergence, and the goodness-of-fit, where the earlier refinement employed weights $w = 1/[\sigma^2(F)]$, with a $(\Delta/\sigma)_{max}$ value of 1.87 and an S value of 0.781 for a final R value of 0.042.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cuesta, R., Arranz Mascarós, P., Low, J. N. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 918–921.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Godino Salido, M. L., Gutiérrez Valero, M. D., Low, J. N. & Glidewell, C. (2003). *Acta Cryst.* In preparation.
Gregson, R. M., Glidewell, C., Ferguson, G. & Lough, A. J. (2000). *Acta Cryst.* **B56**, 39–57.
López Garzón, R., Godino Salido, M. L., Low, J. N. & Glidewell, C. (2003). *Acta Cryst.* In preparation.
Low, J. N., Arranz, P., Cuesta, R., Gutiérrez, M. D. & Glidewell, C. (2003). *Acta Cryst.* **C59**, m21–m24.
Moreno, M. N., Salas, J. M., Colacio, E., Sanchez, M. P. & Nieto, F. (1986). *Acta Cryst.* **C42**, 407–410.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.