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Bis[μ-6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionato-$\kappa^3O^4,N^5:O^5$]-di-μ-aqua-bis{diaqua[6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionato-κ^2N^1,O^2]strontium(II)}: centrosymmetric dimers containing nine-coordinate Sr, linked by multiple hydrogen bonds into a three-dimensional framework

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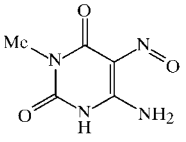
The title complex, $[Sr_2(C_5H_5N_4O_3)_4(H_2O)_6]$, forms centrosymmetric dimers in which one water ligand bridges two Sr centres and in which one of the anionic ligands is bidentate and bonded to just one Sr atom, and the other is tridentate and bridges the two Sr centres within the dimer. The dimeric units are linked by an extensive series of O—H···O, O—H···N and N—H···O hydrogen bonds to form a complex three-dimensional framework.

Comment

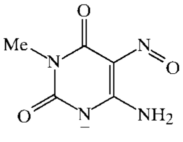
We recently reported the structure, at 150 K, of the dihydrated sodium salt derived from 6-amino-3-methyl-5-nitrosopyrimidine, (I) (Cuesta *et al.*, 2001). In that salt, the Na^+ cations and $(C_5H_4N_4O_3)^-$ anions, denoted *L* and shown as (II) in the *Scheme*, form a one-dimensional coordination polymer in the form of a molecular ladder; the ladders are linked into a continuous three-dimensional framework by a combination of O—H···O and O—H···N hydrogen bonds. Within the ladder, the anion utilizes one amidic O atom and the nitroso N atom to coordinate to a single Na atom, while the other amidic O atom bridges a pair of cations, forming a centrosymmetric Na_2O_2 ring.

Extending our earlier study to a salt of a dication, we have now investigated the title strontium salt, (III). While the stoichiometry of (III) is apparently simple, namely $Sr(L)_2{\cdot}3H_2O$, the two anionic ligands adopt entirely different coordination modes and, while one water molecule acts as a bridging ligand between two metal centres, the other two are bonded simply to one metal atom.

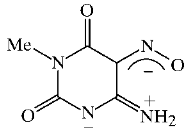
The structures of the two anionic components in (III) are similar but not identical. Each adopts the usual planar conformation, with the nitroso group *trans* to the amidic atoms O*n*4 (*n* = 1 or 2 in the numbering scheme), and each forms an intramolecular N—H···O hydrogen bond with the nitroso O*n*5 atom as acceptor (Fig. 1). The bond distances (Table 1) show a number of metrical features characteristic of 5-nitrosopyrimidines. In particular, the C*n*4—C*n*5 and C*n*5—C*n*6 distances are similar, the difference between the C*n*5—N*n*5 and N*n*5—O*n*5 distances does not exceed 0.05 Å, and the C*n*6—N*n*6 bonds are very short for a single C—N bond between triply connected atoms of these types (Allen *et al.*, 1987). The C—O distances are all typical of those in neutral amides (Allen *et al.*, 1987) and these observations, taken all together, indicate that the delocalized polarized form (II*a*) is a significantly better representation of the anions than the localized form, (II).



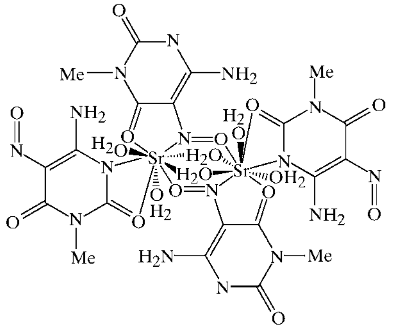
(I)



(II)



(II*a*)



(III)

The coordination complex of (III) (Fig. 1) takes the form of a centrosymmetric dimer, located for the sake of convenience across the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The anion of type 1 (with *n* = 1 in the atom labels) at (*x*, *y*, *z*) forms a bridge between the two Sr centres at (*x*, *y*, *z*) and (1 − *x*, 1 − *y*, 1 − *z*), with the amidic O14 and nitroso N15 atoms coordinated to the Sr atom at (*x*, *y*, *z*) and the nitroso O15 atom bonded to the Sr atom at (1 − *x*, 1 − *y*, 1 − *z*). By contrast, the type 2 anion (with *n* = 2 in the atom labels) is bonded to a single Sr atom *via* the amidic O22 and N21 atoms of the pyrimidine ring.

Effectively orthogonal to the $(SrNO)_2$ ring is an Sr_2O_2 ring, in which water atom O1 acts as a bridging ligand between two Sr centres. The irregular nine-coordination around each Sr centre is completed by two water molecules. We have previously observed examples of metal complexes of substituted 5-nitrosopyrimidines in which the nitroso group acts as a

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η^1 ligand, *via* O, to Na (Low, Moreno Sánchez *et al.*, 2001), K (Low, Arranz *et al.*, 2001) and Sr (Glidewell *et al.*, 2002), as a η^1 ligand, *via* N, to Na (Cuesta *et al.*, 2001), and as a η^2 ligand binding to a single K centre *via* both N and O (Low, Moreno Sánchez *et al.*, 2001); no previous examples of this ligand adopting a μ-bridging mode have been observed. In contrast with the metal-bridging mode of the nitroso group of the type 1 ligand, the nitroso group in the type 2 ligand plays no role in the metal–ligand bonding, although both atoms N25 and O25 act as acceptors of hydrogen bonds (Table 2).

In addition to the N—H···O hydrogen bonds within each anionic ligand of (III), there is a third N—H···O hydrogen bond within the dimeric complex (Fig. 1 and Table 2). Amino atom N26 in the type 2 anion acts as a hydrogen-bond donor, *via* atom H26*A*, to amidic atom O14 in the type 1 anion. This then leaves within the dimer one amino N—H bond and six distinct water O—H bonds, each duplicated by inversion, all of which act as hydrogen-bond donors to acceptors in other dimer units, so linking these units into a single three-dimensional framework. The number of distinct hydrogen bonds leads to some complexity in the framework structure, but the formation of the framework is readily described in terms of a small number of one-dimensional substructures, each in the form of a chain of rings, such that the combination of these substructures necessarily leads to a single framework structure.

The simplest of the hydrogen-bonded substructures in (III) is that running parallel to the [001] direction. Water atom O3 at (x, y, z), which forms part of the complex centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, acts as a hydrogen-bond donor, *via* atom H3*A*, to nitroso atom N25 at ($1 - x$, $1 - y$, $2 - z$), which lies in the dimer centred at $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$, so forming an $R_2^2(14)$ ring centred at $(\frac{1}{2},\frac{1}{2},1)$ (Fig. 2). Propagation of this hydrogen bond by inversion thus generates a chain of spiro-fused rings along [001].

Three hydrogen bonds are involved in chain formation along [010]. Water atoms O1 and O2 at (x, y, z) both act as hydrogen-bond donors, *via* atoms H1*B* and H2*A*, respectively, to amidic atom O12 at (x, $y - 1$, z), which lies in the dimer centred at $(\frac{1}{2},-\frac{1}{2},\frac{1}{2})$. At the same time, water atom O3 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H3*A*, to pyrimidine atom N11 at ($1 - x$, $3 - y$, $1 - z$), which lies in the dimer centred at $(\frac{1}{2},\frac{3}{2},\frac{1}{2})$. Together, these interactions generate a complex chain along [010] (Fig. 3), which consists, in effect, of cages fused along the Sr···Sr vector. The combination of the [010] and [001] chains generates a (100) sheet and this is

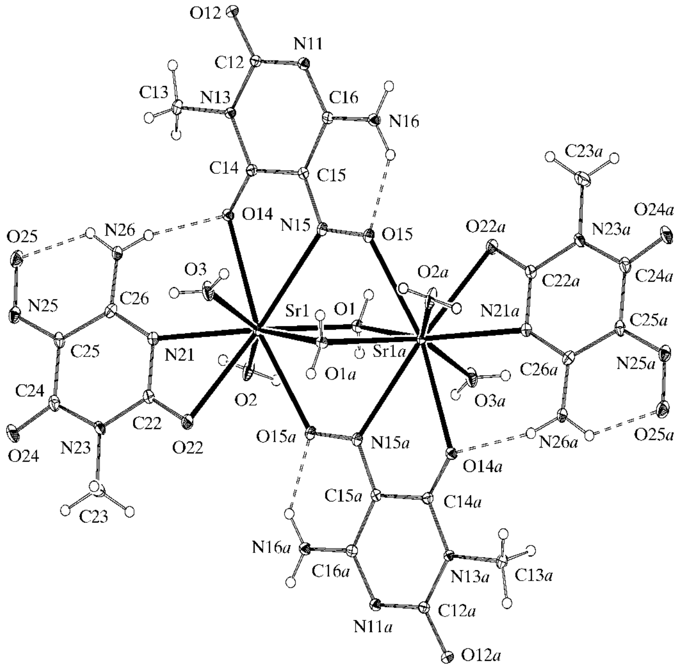

Figure 1

The centrosymmetric dimer complex in (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffix '*a*' are at the symmetry position ($1 - x$, $1 - y$, $1 - z$).

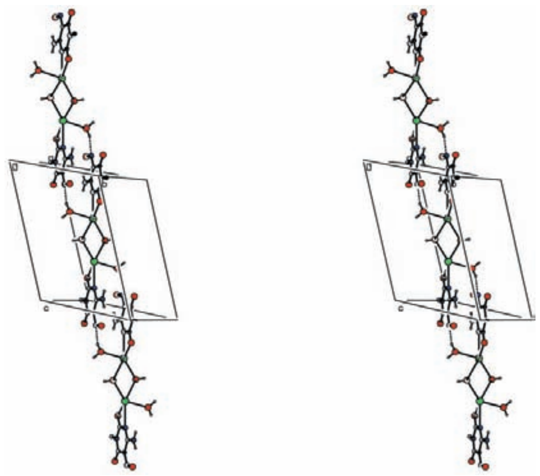

Figure 2

A stereoview of part of the crystal structure of (III), showing the formation of a chain of spiro-fused rings along [001]. For the sake of clarity, the anions of type 1 and the water ligand containing atom O2 have been omitted, as have H atoms bonded to C atoms.

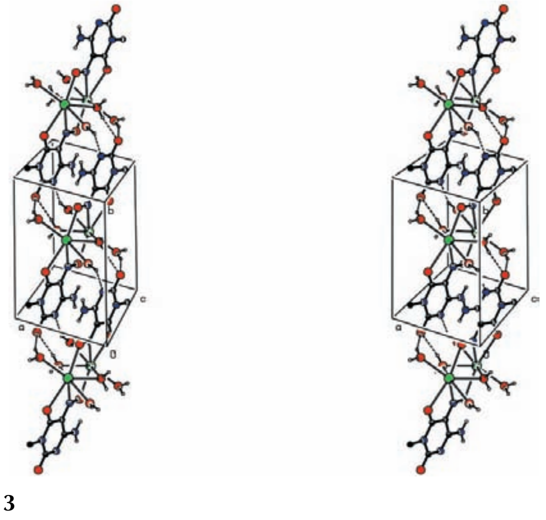

Figure 3

A stereoview of part of the crystal structure of (III), showing the formation of a chain along [010]. For the sake of clarity, the anions of type 2 have been omitted, as have H atoms bonded to C atoms.

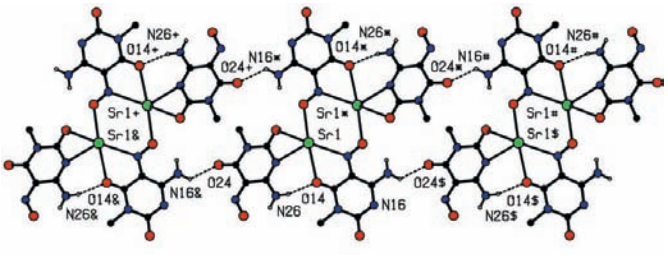

Figure 4
Part of the crystal structure of (III), showing the formation of a chain of edge-fused rings along $[01\overline{1}]$. For the sake of clarity, the unit-cell box and the water ligands have been omitted, as have H atoms bonded to C atoms. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or plus sign (+) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(1 - x, 2 - y, -z)$, $(x, 1 + y, z - 1)$, $(x, y - 1, 1 + z)$ and $(1 - x, -y, 2 - z)$, respectively.

reinforced by the single inter-dimer N—H···O hydrogen bond.

Amino atom N16 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H16*A*, to amidic atom O24 at $(x, 1 + y, z - 1)$, so generating by translation a *C*(11) chain running parallel to the $[01\overline{1}]$ direction. Propagation of this hydrogen bond by translation and inversion generates a chain of edge-fused rings, in which the $(SrNO)_2$ rings alternate with hydrogen-bonded $R_2^2(24)$ rings (Fig. 4). Alternatively, this substructure can be regarded as a molecular ladder, in which a pair of antiparallel *C*(11) chains form the uprights, while the $(SrNO)_2$ rings form the rungs.

Two further O—H···O hydrogen bonds generate chains running parallel to the $[1\overline{1}0]$ and $[10\overline{1}]$ directions. Water atom O1 at (x, y, z), part of the dimer centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, acts as a hydrogen-bond donor, *via* atom H1*A*, to amidic atom O12 at $(-x, 2 - y, 1 - z)$, which lies in the dimer centred at $(-\frac{1}{2},\frac{3}{2},\frac{1}{2})$. Propagation of this hydrogen bond generates a chain of edge-fused rings along $[1\overline{1}0]$, in which Sr_2O_2 rings alternate with hydrogen-bonded $R_2^2(16)$ rings (Fig. 5). Finally, water atom O2 at (x, y, z) acts as a donor, *via* atom H2*B*, to nitroso atom O25 at $(-x, 1 - y, 2 - z)$, which lies in the dimer centred at $(-\frac{1}{2},\frac{1}{2},\frac{3}{2})$, and propagation of this hydrogen bond generates a chain of spiro-fused rings along $[10\overline{1}]$, in which Sr_2O_2 rings alternate with hydrogen-bonded $R_2^2(16)$ rings (Fig. 6). The combination of the [010] and [001] chains with either of the $[1\overline{1}0]$ or $[10\overline{1}]$ chains is itself sufficient to generate a single three-dimensional framework.

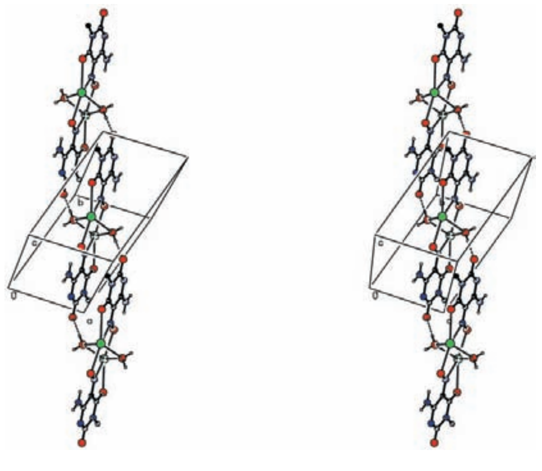

Figure 5
A stereoview of part of the crystal structure of (III), showing the formation of a chain of edge-fused rings along $[1\overline{1}0]$. For the sake of clarity, the anions of type 2 and the water ligands containing atoms O2 and O3 have been omitted, as have H atoms bonded to C atoms.

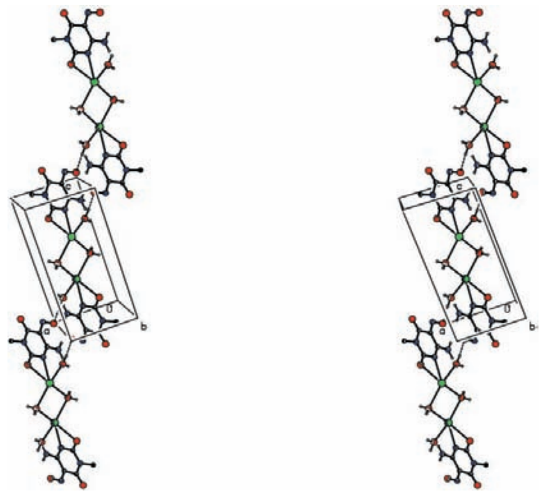

Figure 6
A stereoview of part of the crystal structure of (III), showing the formation of a chain of spiro-fused rings along $[10\overline{1}]$. For the sake of clarity, the anions of type 1 and the water ligands containing atom O3 have been omitted, as have H atoms bonded to C atoms.

Experimental

The salt potassium 6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionate was prepared by the addition of water (20 mmol) to a suspension of 6-amino-3,4-dihydro-3-methyl-2-methoxy-5-nitroso-4-oxopyrimidine (20 mmol) and potassium hydroxide (20 mmol) in methanol (50 ml). The product was filtered off and recrystallized once from water. Analysis found: C 28.6, H 2.5, N 26.6%; $C_5H_5KN_4O_3$ requires: C 28.8, H 2.4, N 26.9%. The title strontium complex, (III), was obtained by adding strontium chloride hexahydrate (1 mmol) to a solution of the potassium salt (2 mmol) in water (40 ml). The orange product was filtered off and washed with cold water and then ethanol. Analysis found: C 24.3, H 3.4, N 21.9%; $C_{20}H_{32}N_{16}O_{18}Sr_2$ requires: C 25.0, H 3.4, N 23.4%. Crystals of (III) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a dilute solution in water.

Crystal data

$[Sr_2(C_5H_5N_4O_3)_4(H_2O)_6]$
$M_r = 959.86$
Triclinic, $P\overline{1}$
$a = 6.9388$ (2) Å
$b = 9.8852$ (2) Å
$c = 14.1962$ (4) Å
$\alpha = 69.965$ (2)°
$\beta = 77.518$ (2)°
$\gamma = 72.361$ (2)°
$V = 864.91$ (4) Å^3

$Z = 1$
$D_x = 1.843$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3883 reflections
$\theta = 3.1$–27.5°
$\mu = 3.19$ mm^{-1}
$T = 120$ (2) K
Block, orange
0.30 × 0.28 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\rm min} = 0.391$, $T_{\rm max} = 0.449$
12 233 measured reflections
3883 independent reflections
3540 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\rm max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.068$
$S = 1.00$
3883 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.7547P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.345 (3)	N21—C22	1.362 (3)
C12—N13	1.405 (3)	C22—N23	1.406 (3)
N13—C14	1.382 (3)	N23—C24	1.382 (3)
C14—C15	1.457 (3)	C24—C25	1.465 (3)
C15—C16	1.445 (3)	C25—C26	1.447 (3)
C16—N11	1.344 (3)	C26—N21	1.331 (3)
C12—O12	1.250 (2)	C22—O22	1.229 (3)
C13—N13	1.475 (3)	N23—C23	1.468 (3)
C14—O14	1.232 (3)	C24—O24	1.233 (3)
C15—N15	1.330 (3)	C25—N25	1.330 (3)
N15—O15	1.290 (2)	N25—O25	1.298 (2)
C16—N16	1.321 (3)	C26—N26	1.326 (3)
Sr1—O14	2.7357 (15)	Sr1—O1	2.6916 (15)
Sr1—N15	2.7946 (18)	Sr1—O1$^{\rm i}$	2.7127 (15)
Sr1—O15$^{\rm i}$	2.6231 (15)	Sr1—O2	2.5331 (16)
Sr1—N21	2.6654 (17)	Sr1—O3	2.5250 (16)
Sr1—O22	2.7175 (15)	Sr1···Sr1$^{\rm i}$	4.2169 (4)
O15—N15—Sr1	120.69 (12)	O1—Sr1—O1$^{\rm i}$	77.43 (5)
N15—O15—Sr1$^{\rm i}$	122.83 (12)	Sr1—O1—Sr1$^{\rm i}$	102.57 (5)
O15$^{\rm i}$—Sr1—N15	113.82 (5)		

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

Compound (III) is triclinic; space group $P\overline{1}$ was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances of 0.98 Å, N—H distances of 0.88 Å and O—H distances in the range 0.84–0.88 Å.

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, 2002); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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

D—H···A	D—H	H···A	D···A	D—H···A
N16—H16A···O24$^{\rm i}$	0.88	2.13	2.776 (3)	129
N16—H16B···O15	0.88	1.94	2.594 (3)	130
N26—H26A···O14	0.88	2.11	2.964 (3)	164
N26—H26B···O25	0.88	1.94	2.595 (3)	130
O1—H1A···O12$^{\rm ii}$	0.84	1.94	2.772 (2)	174
O1—H1B···O12$^{\rm iii}$	0.84	2.09	2.920 (2)	169
O2—H2A···O12$^{\rm iii}$	0.88	2.02	2.846 (2)	156
O2—H2B···O25$^{\rm iv}$	0.88	1.82	2.700 (2)	173
O3—H3A···N25$^{\rm v}$	0.88	2.02	2.871 (3)	163
O3—H3B···N11$^{\rm vi}$	0.88	2.00	2.806 (3)	152

Symmetry codes: (i) $x, 1 + y, z - 1$; (ii) $-x, 2 - y, 1 - z$; (iii) $x, y - 1, z$; (iv) $-x, 1 - y, 2 - z$; (v) $1 - x, 1 - y, 2 - z$; (vi) $1 - x, 2 - y, 1 - z$.

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1602). Services for accessing these data are described at the back of the journal.

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