Potassium N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)-(S)-aspartate N-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)-(S)-aspartic acid 4.88-hydrate: a two-dimensional coordination polymer

Rafael Cuesta,[a] Christopher Glidewell,[b]* Rafael López[a] and John N. Low[c]†

[a]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [b]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland, and [c]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

In the title compound, $K^+ \cdot C_9H_{10}N_5O_6{}^- \cdot C_9H_{11}N_5O_6 \cdot 4.88H_2O$, the cations are eight-coordinate. There is a one-dimensional coordination-polymer substructure, built from K and O atoms only, in the form of chains of distorted confacial octahedra, and these are linked into sheets by the neutral organic ligand. The sheets are linked into a single framework by a combination of N—H···O and O—H···O hydrogen bonds.

Comment

We have reported recently the molecular and supramolecular structures of the hydrated potassium complexes derived from the anionic ligands L^1 and L^2 (see *Scheme*). In $[K(L^1)(H_2O)]$, chains of spiro-fused K_2O_2 rings are linked into sheets by means of the unusual η^2-coordination of the nitroso substituent, and the coordination-polymer sheets are linked into a three-dimensional framework by hydrogen bonds (Low, Moreno Sánchez *et al.*, 2001). In $[K(L^2)(H_2O)]$, by contrast, the coordination polymer is three-dimensional; K_2O_2 rings are again present, but they are isolated from one another and the nitroso substituent adopts the more usual η^1-coordination mode (Low, Arranz *et al.*, 2001)

Continuing this investigation, we have now turned to an analogous ligand, L^3, containing a dicarboxylic acid side chain, and we report here the structure of the hydrated potassium complex, (I). The constitution of (I) is that of an acid salt,

† Postal address: Department of Electrical Engineering and Physics, University of Dundee, Dundee DD1 4HN, Scotland.

$[K(L^3)(HL^3)(H_2O)_{4.88}]$, in which the carboxyl group of the HL^3 unit is not ionized. There are three fully occupied water sites (*viz.* those containing atoms O1–O3, including one molecule that is directly coordinated to the cation) and three partially occupied sites (*viz.* those containing atoms O4–O6; Fig. 1). The anionic ligand (containing atoms N11, C12 *etc.*) is coordinated to the K^+ cation *via* both atom O14 and atom N15, while atom O14 is also coordinated to the cation at $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$. The neutral organic HL^3 ligand is directly coordinated to the cation only *via* atom O24, which also coordinates to the K^+ cation at $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$; likewise water atom O1 at (x, y, z) is coordinated to cations at both (x, y, z) and $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$. The eight-coordination of the cation is completed by carboxyl atom O224 at $(x, -1 + y, z)$, and a hydrogen bond formed between atoms O1 and N25 effectively prevents this N atom from coordinating to the cation (Fig. 1), so that the coordination behaviour of the neutral HL^3 ligand differs from that of the anionic $(L^3)^-$ ligand. The remaining water molecules are linked to the coordination complex by means of hydrogen bonds, primarily of the O—H···O type, but including one of the N—H···O type (Fig. 1 and Table 2).
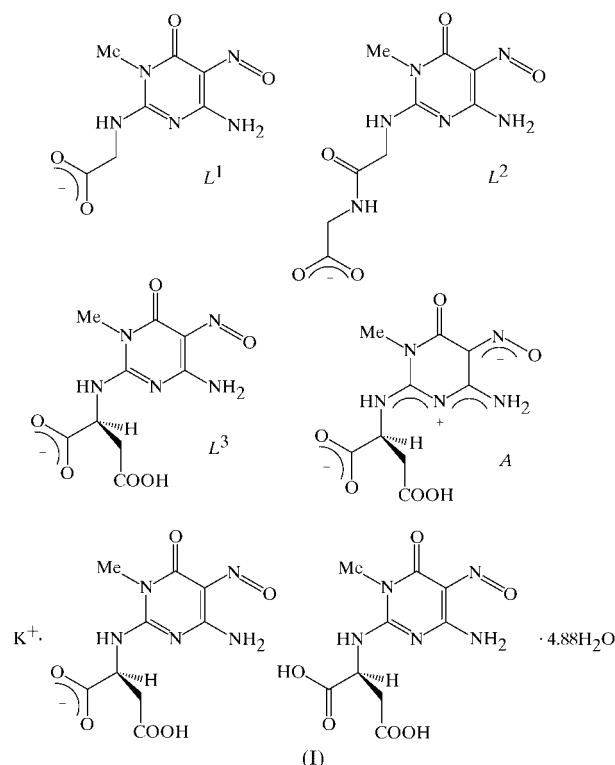
In both organic ligands, the ring dimensions (Table 1) display to an extreme degree the electronic polarization that is now a familiar feature of compounds containing this type of substituted oxopyrimidinyl ring (Low *et al.*, 2000; Low, Arranz *et al.*, 2001; Low, Moreno Sánchez *et al.*, 2001). In particular, the exocyclic Cn6—Nn6 bonds ($n = 1$ or 2) are both shorter than those typically found in metal complexes of ligands of this general type (Low, Moreno Sánchez *et al.*, 2001). Overall,

the ring dimensions point to the importance of the polarized form A at the expense of the classically localized form of L^3 (see *Scheme*).

The C—O distances in the carboxyl groups are consistent with the H-atom locations deduced from difference maps. Thus, at both atom C124 and atom C224, the C—O distances are typical of those in un-ionized carboxyl groups (Allen *et al.*, 1987), while the two distances at atom C122 are very similar and are consistent with the presence of a fully ionized carboxylate unit. At atom C222, on the other hand, the difference between the two C—O distances is less than that typically found in un-ionized carboxyl groups (mean value 0.122 Å; Allen *et al.*, 1987). While in both organic ligands there is complete synclinal staggering about the Cn21—Cn23 bonds (n = 1 or 2), the skeletal conformations about the Nn1—Cn21 bonds are quite different, being synclinal in the anionic ligand and anticlinal in the neutral ligand; this latter conformation may be influenced by the intramolecular N22—H22···O223 hydrogen bond.

Since atoms O1, O14 and O24 at (x, y, z) all bridge the pair of cations at (x, y, z) and $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$, these interactions give rise to a one-dimensional coordination polymer, which takes the form of a chain of distorted confacial octahedra (Fig. 2) that runs parallel to the [100] direction and is generated by the 2_1 screw axis along $(x, \frac{3}{4}, \frac{1}{2})$. A second such chain, generated by the 2_1 screw axis along $(x, \frac{1}{4}, 0)$, passes through the unit cell. In each domain of z, the [100] chains are linked into (001) sheets. The final coordination site of the cation at (x, y, z) is occupied by carboxyl atom O224 from the neutral organic ligand at $(x, -1 + y, z)$, so forming by translation a $C_2^1(10)$ motif (Starbuck *et al.*, 1999) running parallel to the [010] direction (Fig. 3). The combination of the [100] and [010] chains generates a (001) sheet, two of which pass through each unit cell.
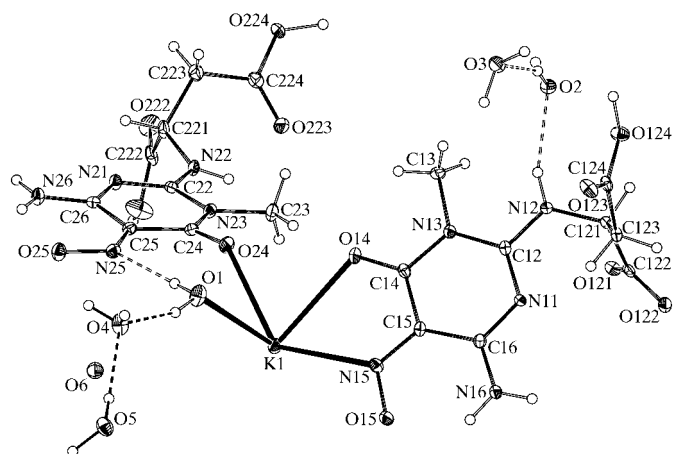
In addition to three intramolecular N—H···O hydrogen bonds, each of which forms an $S(6)$ motif (Bernstein *et al.*, 1995), there are intermolecular O—H···O, O—H···N and N—H···O hydrogen bonds in the asymmetric unit (Fig. 1 and Table 2). There are also a substantial number of hydrogen bonds linking these molecular aggregates together, and we discuss here just three points concerning the bonds that have structural significance. First, the three O—H···O hydrogen bonds having carboxyl donors are characterized by short O···O distances, in every case less than 2.60 Å. In particular, the hydrogen bond having anionic nitroso atom O15 as acceptor has an O···O distance of only 2.502 (3) Å, which is comparable to those observed for such hydrogen bonds in neutral *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)amino acids; moreover the C15—N15 and N15—O15 distances associated with this hydrogen bond agree with the correlation established previously between such distances and the O···O hydrogen-bond distances (Low *et al.*, 2000). Secondly, despite the number of un-ionized carboxyl groups present in the structure, these generate neither of the two hydrogen-bonded motifs [$C(4)$ and $R_2^2(8)$] that are so characteristic of simple carboxylic acids; indeed, there is no hydrogen bond present in which both donor and acceptor are components of neutral carboxyl groups. There is, however, a single example, namely O124—H124···O121(1 + x, y, z), in which the ionized carboxylate unit provides the acceptor. Thirdly, a number of the hydrogen bonds serve to link the (001) sheets into a single continuous framework, and just two examples suffice to demonstrate this behaviour. Atom N16 at (x, y, z) lies in the (001) sheet containing the 2_1 screw axes at $z = \frac{1}{2}$ and acts as a hydrogen-bond donor, *via* atom H16A, to water atom O2 at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, which lies in the sheet containing the 2_1 axes at $z = 0$. At the same time, atom N26 at

Figure 1
The independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The water molecules based on atoms O4 and O5 have occupancies of 0.883 (5), and atom O6 has an occupancy of 0.117 (5). H atoms bonded to atom O6 could not be located (see text).
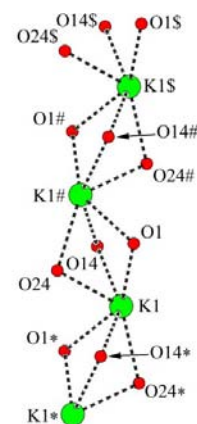

Figure 2
Part of the crystal structure of (I), showing the formation of the coordination polymer along [100] built from K and O atoms only. For clarity, the unit-cell box has been omitted. Atoms marked with an asterisk (*), a hash (#) or a dollar sign ($) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$, $(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$ and $(1 + x, y, z)$, respectively.
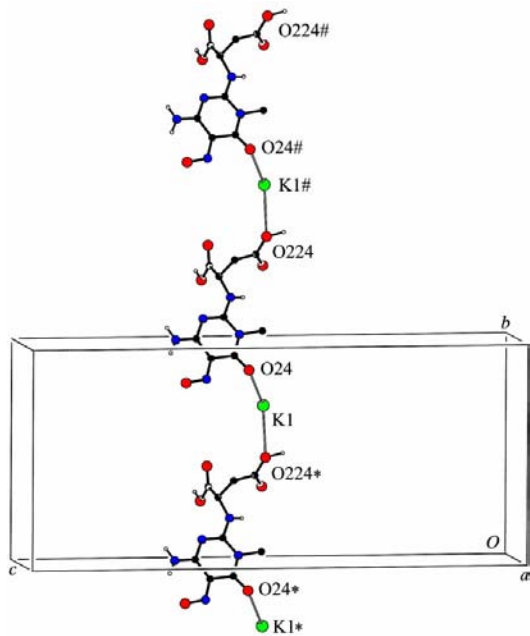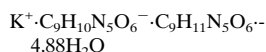
Figure 3
Part of the crystal structure of (I), showing the formation of a chain along [010] built from cations and neutral organic ligands only. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, -1 + y, z)$ and $(x, 1 + y, z)$, respectively.

(x, y, z) acts as a hydrogen-bond donor, *via* atom H26A, to carboxylate atom O121 at $(\frac{1}{2} - x, 2 - y, \frac{1}{2} + z)$, which lies in the sheet containing the 2_1 axes at $z = 1$. Two O—H···O hydrogen bonds, involving water atoms O2 and O5 as donors, reinforce the linking of the (001) sheets (Table 2).

Experimental

The title compound was obtained by adding 6-amino-3,4-dihydro-3-methyl-2-methoxy-5-nitroso-4-oxopyrimidine (3.5 mmol) to a solution of potassium (S)-aspartate (3.5 mmol) in methanol (40 ml). The mixture was stirred at 315 K for 2 d and a pink solid was removed by filtration. The filtrate was evaporated to dryness, the residue was dissolved in water and the pH of the resulting solution was adjusted to 2.15 by dropwise addition of aqueous HCl. After two weeks at room temperature, red crystals of the product were collected by filtration and washed with ethanol. Analysis found: C 31.3, H 4.9, N 20.3%; $C_{18}H_{30.76}KN_{10}O_{16.88}$ requires: C 31.0, H 4.5, N 20.1%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample.

Crystal data

$K^+ \cdot C_9H_{10}N_5O_6{}^- \cdot C_9H_{11}N_5O_6 \cdot$ 4.88H$_2$O	$D_x = 1.591$ Mg m^{-3}
$M_r = 696.52$	Mo $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	Cell parameters from 6543 reflections
$a = 7.4986 (1)$ Å	$\theta = 3.1$–$27.5°$
$b = 13.0997 (2)$ Å	$\mu = 0.28$ mm^{-1}
$c = 29.5866 (6)$ Å	$T = 120 (2)$ K
$V = 2906.27 (8)$ Å^3	Needle, red
$Z = 4$	$0.35 \times 0.10 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer	6543 independent reflections
φ scans, and ω scans with κ offsets	5256 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.071$
(*DENZO–SMN*; Otwinowski & Minor, 1997)	$\theta_{max} = 27.5°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.941$, $T_{max} = 0.986$	$k = -17 \rightarrow 14$
21 931 measured reflections	$l = -37 \rightarrow 38$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$\Delta\rho_{max} = 0.66$ e Å^{-3}
$wR(F^2) = 0.114$	$\Delta\rho_{min} = -0.58$ e Å^{-3}
$S = 1.04$	Absolute structure: Flack (1983),
6543 reflections	2893 Friedel pairs
422 parameters	Flack parameter = 0.00 (5)
H-atom parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2$ $+ 1.9469P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Crystals of (I) are orthorhombic and the space group $P2_12_12_1$ was assigned uniquely from the systematic absences. H atoms bonded to C or N atoms were treated as riding atoms, with C—H distances of 0.98 (CH$_3$), 0.99 (CH$_2$) and 1.00 Å (CH), and N—H distances of 0.88 Å. Water H atoms were located from difference maps and were initially constrained to have O—H distances in each molecule equal to the average distance found for that molecule from the difference maps; these H atoms were finally treated as riding using the AFIX3 command in *SHELXL*97 (Sheldrick, 1997), giving O—H distances of 0.90–0.98 Å. Carboxyl H atoms were treated as riding atoms, the C—H distances of 0.99–1.12 Å being deduced from difference maps. At a late stage in the refinement, it became apparent that there was a partially occupied water O-atom site, denoted O6, whose distances from the sites denoted O4 and O5 were such that site O6 could not be occupied at the same time as O4 and O5; sites O4 and O5 could themselves be concurrently occupied, provided that site O6 was unoccupied. This situation was modelled by assigning a common site

Table 1
Selected geometric parameters (Å, °).

K1—O1	2.758 (2)	K1—O1^{vi}	2.885 (3)
K1—O14	2.944 (2)	K1—O14^{vi}	2.832 (2)
K1—O24	2.709 (2)	K1—O24^{vi}	2.838 (2)
K1—N15	2.902 (3)	K1—O224^{xi}	3.085 (2)
N11—C12	1.321 (4)	N21—C22	1.325 (4)
C12—N13	1.386 (4)	C22—N23	1.381 (4)
N13—C14	1.394 (4)	N23—C24	1.390 (4)
C14—C15	1.466 (4)	C24—C25	1.458 (4)
C15—C16	1.459 (4)	C25—C26	1.445 (4)
C16—N11	1.338 (4)	C26—N21	1.342 (4)
C12—N12	1.338 (4)	C22—N22	1.329 (4)
N13—C13	1.466 (4)	N23—C23	1.470 (4)
C14—O14	1.231 (4)	C24—O24	1.226 (4)
C15—N15	1.324 (4)	C25—N25	1.337 (4)
O15—N15	1.300 (3)	N25—O25	1.292 (3)
C16—N16	1.309 (4)	C26—N26	1.310 (4)
C122—O121	1.275 (4)	C222—O221	1.287 (4)
C122—O122	1.246 (4)	C222—O222	1.228 (4)
C124—O123	1.211 (4)	C224—O223	1.220 (4)
C124—O124	1.330 (4)	C224—O224	1.316 (4)
N11—C12—N12—C121	2.0 (4)	N21—C22—N22—C221	15.5 (5)
C12—N12—C121—C122	57.6 (4)	C22—N22—C221—C222	−116.6 (3)
C12—N12—C121—C123	−71.3 (4)	C22—N22—C221—C223	117.9 (3)
N12—C121—C122—O121	38.6 (4)	N22—C221—C222—O221	36.3 (4)
N12—C121—C123—C124	−64.1 (3)	N22—C221—C223—C224	60.5 (4)
C121—C123—C124—O123	147.8 (3)	C221—C223—C224—O223	−17.3 (5)

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

metal-organic compounds

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N12—H12$\cdots$O2	0.88	2.02	2.852 (3)	157
O124—H124$\cdots$O121[i]	1.12	1.45	2.570 (3)	172
N16—H16$A\cdots$O2[ii]	0.88	2.04	2.910 (3)	170
N16—H16$B\cdots$O15	0.88	1.99	2.634 (3)	129
N22—H22$\cdots$O223	0.88	2.23	2.781 (3)	120
O221—H21$E\cdots$O5[iii]	0.99	1.55	2.534 (4)	174
O224—H224$\cdots$O15[iv]	1.08	1.44	2.502 (3)	167
N26—H26$A\cdots$O121[v]	0.88	2.02	2.875 (3)	164
N26—H26$B\cdots$O25	0.88	2.00	2.637 (3)	129
N26—H26$B\cdots$O123[vi]	0.88	2.25	2.989 (3)	141
O1—H1$A\cdots$N25	0.90	2.06	2.949 (3)	172
O1—H1$B\cdots$O4	0.90	1.89	2.762 (3)	163
O2—H2$A\cdots$O3	0.90	2.03	2.881 (3)	158
O2—H2$B\cdots$O122[vii]	0.90	2.02	2.918 (3)	174
O3—H3$A\cdots$O121[i]	0.98	1.86	2.771 (3)	154
O3—H3$B\cdots$O25[viii]	0.98	1.76	2.723 (3)	169
O4—H4$A\cdots$O222[ix]	0.90	1.80	2.687 (4)	171
O4—H4$B\cdots$O3[vi]	0.90	1.80	2.672 (3)	164
O5—H5$A\cdots$O122[x]	0.98	1.81	2.719 (3)	153
O5—H5$B\cdots$O4	0.98	1.84	2.741 (4)	151

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

occupancy to sites O4 and O5 while tying the occupancy of site O6 to this common occupancy. The resulting occupancy factors are 0.883 (5) for O4 and O5, and 0.117 (5) for O6, and these occupancy values are associated with satisfactory displacement parameters.

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).

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