

Barium bis[6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionate] trihydrate: coordination polymer chains linked by hydrogen bonds

Rafael López Garzón,^a M. Luz Godino Salido,^a John N. Low^{b†} and Christopher Glidewell^{c*}

^aDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

Received 28 April 2003

Accepted 6 May 2003

Online 31 May 2003

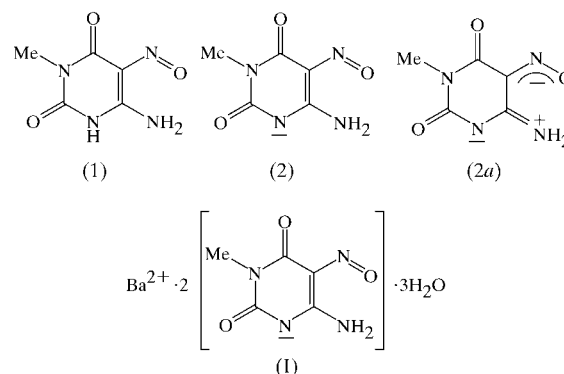
The title complex, *catena*-poly[[triaquabarium(II)]-di- μ -6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dionate], [Ba(C₅H₅N₄O₃)₂(H₂O)₃]_n, forms a coordination polymer chain in which the two distinct anions use different ligating atoms to bridge pairs of cations. Adjacent pairs of cations are also linked by pairs of bridging water molecules. The chains are linked into a single three-dimensional framework by an extensive series of hydrogen bonds.

Comment

We have reported recently the molecular and supramolecular structures of the hydrated sodium and strontium salts that are derived from 6-amino-3-methyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dione, (1). The cations and the C₅H₅N₄O₃⁻ anions [denoted *L* and shown as (2) in the *Scheme*] in the sodium salt, Na(*L*)·2H₂O, constitute a one-dimensional coordination polymer in the form of a molecular ladder, and the ladders are linked into a continuous three-dimensional framework by a combination of O—H···O and O—H···N hydrogen bonds (Cuesta *et al.*, 2001). Within the ladder, the anion uses one amide O atom and the nitroso N atom to coordinate to a single Na atom, while the other amide O atom bridges a pair of cations, thus forming a centrosymmetric Na₂O₂ ring. By contrast, the Sr salt, of composition Sr(*L*)₂·3H₂O, forms a centrosymmetric dimer in which the two *L* ligands adopt entirely different coordination modes; one water ligand bridges two Sr centres, and one of the anionic ligands is bidentate and bonded to just one Sr atom, while the other is tridentate and bridges the two Sr-atom centres in the dimer.

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

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 (Low *et al.*, 2003).



Continuing this study, we report here the structure of the hydrated barium salt, (I), of *L*, whose composition, Ba(*L*)₂·3H₂O, is analogous to that of the Sr salt. While the structure of (I) (Fig. 1) is different from the structures of both the Na and the Sr complexes of *L*, it shares certain features with both of them. Complex (I) resembles Na(*L*)·2H₂O in that both form one-dimensional coordination polymers, but differs from it in containing two distinct anions exhibiting different coordination behaviour and in forming a chain of spiro-fused rings rather than edge-fused rings. Complex (I) resembles Sr(*L*)₂·3H₂O in forming centrosymmetric *M*₂(anion)₂ and *M*₂(H₂O)₂ rings, but differs from it in forming a coordination polymer containing ten-coordinate *M* (Fig. 2) rather than a finite centrosymmetric dimer containing nine-coordinate *M*.

The structures of the two independent anions are similar but not identical; each adopts the usual planar conformation, with the nitroso group *trans* to the amide *On*4 atoms (*n* = 1 or 2), and each forms an intramolecular N—H···O hydrogen bond with the nitroso *On*5 atom as acceptor (Fig. 1). The anions show a number of the geometric characteristics of 5-nitrosopyrimidines (Low *et al.*, 2000; Low, Arranz, Cobo,

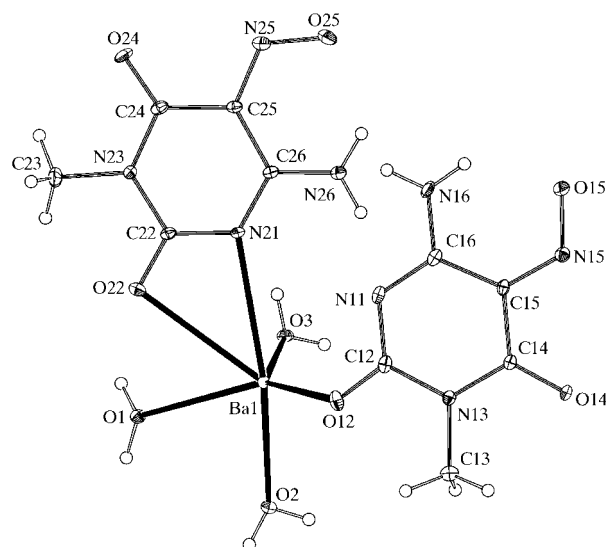


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Fontecha, Godino, López, Cannon *et al.*, 2001; Low, Arranz, Cobo, Fontecha, Godino, López & Glidewell, 2001; Low, Cannon *et al.*, 2001; Low, Moreno *et al.*, 2001). In particular, the C4–C5 and C5–C6 distances are very similar, the difference between the C5–N5 and N5–O5 distances is less than 0.065 Å, and the C6–N6 bond is very short for a single C–N bond between three-connected atoms (Allen *et al.*, 1987). While the similar C2–O2 and C4–O4 distances are both typical of those in neutral amides (Allen *et al.*, 1987), the N1–C6 bond is somewhat shorter than the N1–C2 bond. These observations taken together indicate polarization of the electronic structure, so that (2a) is a significantly better representation than (2) (see *Scheme*).

In forming the polymer chain in (I), the type 1 anion (containing N11, N13 *etc.*) uses two O atoms (O12 and O14) to coordinate to two different Ba atoms, reinforced by weak coordination of nitroso atom N15, while the type 2 anion (containing N21, N23 *etc.*) uses atoms O22 and N21 to coordinate to a pair of Ba atoms different from those coordinated by the type 1 anion (Table 1). Thus, in the type 1 anion at (x, y, z) , atoms O12 and O14 are bonded to Ba atoms at (x, y, z) and $(1 - x, 1 - y, -z)$, respectively, while in the type 1 anion at $(1 - x, 1 - y, -z)$, atoms O12 and O14 are bonded to Ba atoms at $(1 - x, 1 - y, -z)$ and (x, y, z) , respectively. In this manner, a centrosymmetric $R_4^2(12)$ ring (Starbuck *et al.*, 1999)

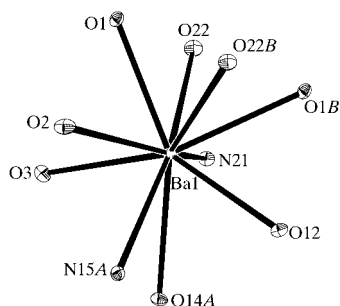


Figure 2

The ten-coordination of barium in (I). Atoms marked with suffixes *A* and *B* are at the symmetry positions $(1 - x, 1 - y, -z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

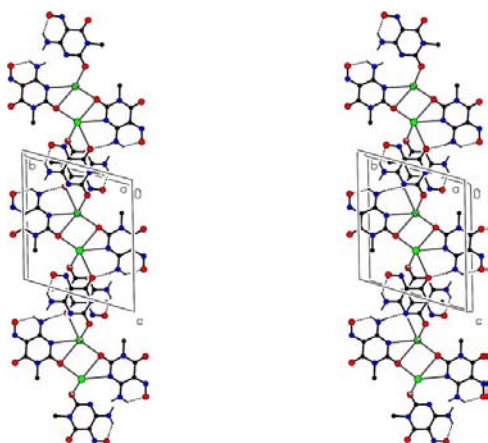


Figure 3

Stereoview of part of the crystal structure of (I), showing the formation of the coordination polymer chain along $(\frac{1}{2}, \frac{1}{2}, z)$.

is formed, centred at $(\frac{1}{2}, \frac{1}{2}, 0)$. In the type 2 anion at (x, y, z) , atoms N21 and O22 are bonded to Ba atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, respectively, forming a centrosymmetric $R_4^2(8)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation by inversion of these two ring motifs thus generates a chain of spiro-fused rings running parallel to the [001] direction (Fig. 3), with $R_4^2(8)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + n)$ ($n = \text{zero or integer}$) and $R_4^2(12)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$ ($n = \text{zero or integer}$). The chain is reinforced by two hydrogen bonds; atoms N26 and O2 at (x, y, z) act as hydrogen-bond donors, *via* atoms H26A and H2B, to atoms O14 and O15, respectively, both at $(1 - x, 1 - y, -z)$.

Almost orthogonal to the $R_4^2(8)$ rings are centrosymmetric Ba_2O_2 rings containing water atom O1, where atom O1 at (x, y, z) is coordinated to Ba atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$. This feature thus resembles the Sr_2O_2 rings formed in the $\text{Sr}(L)_2 \cdot 3\text{H}_2\text{O}$ complex (Low *et al.*, 2003). The coordination of the Ba atom at (x, y, z) is completed by the two water molecules containing atoms O2 and O3, both of which are bonded to a single cation, and by weak interactions with atom O22 in the type 2 cation at (x, y, z) and atom N15 in the type 1 cation at $(1 - x, 1 - y, -z)$, so giving a tenfold coordination (Fig. 2). This may be contrasted with the near-octahedral six-coordination in $\text{Na}(L) \cdot 2\text{H}_2\text{O}$ and the nine-coordination in $\text{Sr}(L)_2 \cdot 3\text{H}_2\text{O}$.

There is just one coordination polymer chain running through each unit cell, and adjacent chains are linked by an extensive series of O–H...O, O–H...N and N–H...O hydrogen bonds (Table 2) to form a single three-dimensional framework. The formation of this framework is readily analyzed in terms of several one-dimensional substructures.

Water atom O1 at (x, y, z) lies in a Ba_2O_2 ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and acts as a hydrogen-bond donor to both water atom O2 and water atom O3 at $(-x, 1 - y, 1 - z)$. These water molecules are directly coordinated to the Ba atom at $(-x, 1 - y, 1 - z)$, which itself lies in the Ba_2O_2 ring centred at $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation of these hydrogen bonds by translation and inversion leads to the formation of a chain of rings running parallel to the [100] direction (Fig. 4). This chain contains Ba_2O_2 rings centred at $(\frac{1}{2} + n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$), and rectangular prismatic cages built from two Ba atoms and six water molecules centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$). This [100] chain is reinforced by the single O–H...N hydrogen

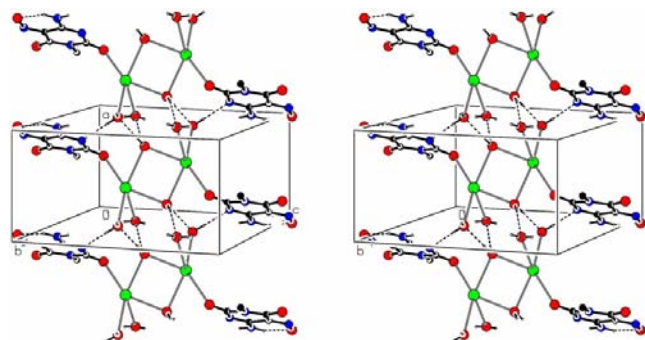


Figure 4

Stereoview of part of the crystal structure of (I), showing the formation of the hydrogen-bonded chain along $(x, \frac{1}{2}, \frac{1}{2})$.

bond in the structure, in which water atom O3 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H3B, to pyrimidine atom N11 in the type 1 anion at $(-1 + x, y, z)$ (Fig. 4).

Water atom O3 at (x, y, z) is directly coordinated to the Ba atom at (x, y, z) . This water molecule acts as a donor, *via* atom H3A, to both atom O24 and atom N25 in the type 2 anion at $(1 - x, 2 - y, 1 - z)$ in an effectively planar three-centre O—H \cdots (N,O) hydrogen bond. This type 2 anion is directly coordinated to the Ba atom at $(1 - x, 2 - y, 1 - z)$, which forms part of a Ba₂O₂ ring centred at $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$. Propagation of this three-centre hydrogen bond thus generates a chain of rings running parallel to [010], containing Ba₂O₂ rings centred at $(\frac{1}{2}, \frac{1}{2} + n, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_6^4(14)$ rings (Bernstein *et al.*, 1995; Starbuck *et al.*, 1999) centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 5).

The chains along [100], [010] and [001] (Figs. 3–5) are sufficient to generate a single three-dimensional framework. However, the formation of these chains does not fully utilize all of the intermolecular hydrogen bonds, and the final two bonds serve to reinforce the framework by forming a chain running parallel to the [110] direction. Amino atom N16 in the type 1 anion at (x, y, z) acts as a hydrogen-bond donor to atom

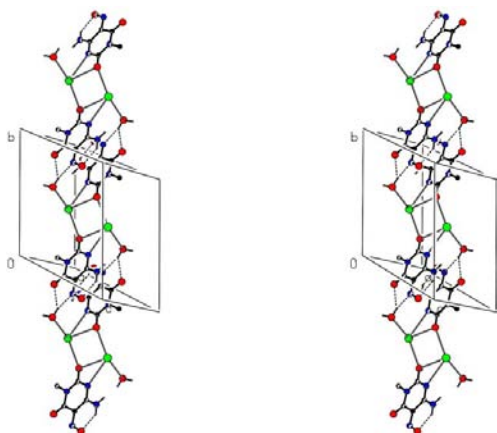


Figure 5
Stereoview of part of the crystal structure of (I), showing the formation of the chain of rings along $(\frac{1}{2}, y, \frac{1}{2})$.

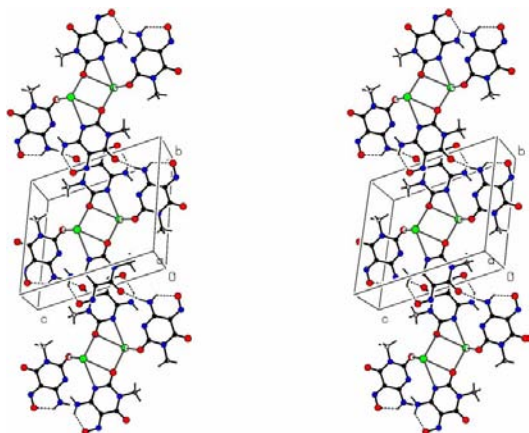


Figure 6
Stereoview of part of the crystal structure of (I), showing the formation of the chain of rings parallel to [110].

O24 in the type 2 anion at $(2 - x, 2 - y, 1 - z)$, so generating a chain containing Ba₂O₂ rings centred at $(\frac{1}{2} + n, \frac{1}{2} + n, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_6^4(24)$ rings centred at $(n, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 6). This [110] chain is itself reinforced by an O—H \cdots O hydrogen bond in which water atom O2 at (x, y, z) acts as a donor, *via* atom H2A, to atom O25 in the type 2 anion at $(-1 + x, -1 + y, z)$.

Experimental

The title compound was obtained by adding barium chloride trihydrate (3 mmol) to a solution of the corresponding potassium uracilate, K(L) (1 mmol), in methanol/water (40 ml, 9:1 *v/v*). Slow evaporation of this solution gave crystals, which were dried over CaCl₂ for two weeks. Crystals suitable for single-crystal X-ray diffraction were selected directly from the prepared sample. Analysis found: C 21.7, H 2.8, N 20.9%; C₁₀H₁₆BaN₈O₉ requires: C 22.7, H 3.0, N 21.2%.

Crystal data

[Ba(C₅H₅N₄O₃)₂(H₂O)₃]
M_r = 529.65
 Triclinic, $P\bar{1}$
a = 6.7594 (1) Å
b = 11.2513 (3) Å
c = 12.6048 (2) Å
 α = 106.467 (2)°
 β = 92.911 (1)°
 γ = 99.935 (1)°
V = 900.46 (3) Å³

Z = 2
D_x = 1.953 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 3946 reflections
 θ = 2.9–27.5°
 μ = 2.27 mm⁻¹
T = 120 (2) K
 Block, pink
 0.32 × 0.24 × 0.16 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} = 0.519, *T_{max}* = 0.699
 11 514 measured reflections

3946 independent reflections
 3892 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
 θ_{max} = 27.5°
h = -8 → 8
k = -14 → 14
l = -16 → 15

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.073$
S = 1.15
 3946 reflections
 255 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.9783P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.22 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Ba1—O1	2.7852 (19)	Ba1—N21	2.938 (2)
Ba1—O2	2.910 (2)	Ba1—N15 ⁱ	3.023 (2)
Ba1—O3	2.7966 (19)	Ba1—O1 ⁱⁱ	2.8836 (19)
Ba1—O12	2.800 (2)	Ba1—O14 ⁱ	2.9501 (19)
Ba1—O22	3.028 (2)	Ba1—O22 ⁱⁱ	2.7809 (19)
N11—C12	1.358 (4)	N21—C22	1.349 (4)
C12—N13	1.419 (3)	C22—N23	1.401 (3)
N13—C14	1.377 (3)	N23—C24	1.379 (4)
C14—C15	1.459 (4)	C24—C25	1.457 (4)
C15—C16	1.453 (4)	C25—C26	1.449 (4)
C16—N11	1.329 (4)	C26—N21	1.338 (3)
C12—O12	1.234 (3)	C22—O22	1.239 (3)
C13—N13	1.464 (3)	N23—C23	1.464 (4)
C14—O14	1.230 (3)	C24—O24	1.228 (3)
C15—N15	1.332 (4)	C25—N25	1.335 (3)
N15—O15	1.291 (3)	N25—O25	1.295 (3)
C16—N16	1.328 (4)	C26—N26	1.316 (4)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O3 ⁱⁱⁱ	0.90	1.88	2.735 (3)	157
O1—H1B...O2 ⁱⁱⁱ	0.90	2.11	2.918 (3)	150
O2—H2A...O25 ^{iv}	0.82	1.96	2.761 (3)	167
O2—H2B...O15 ⁱ	0.82	2.01	2.781 (3)	156
O3—H3A...N25 ^v	0.82	2.19	2.934 (3)	151
O3—H3A...O24 ^v	0.82	2.34	2.967 (3)	133
O3—H3B...N11 ^{vi}	0.82	2.11	2.924 (3)	173
N16—H16A...O24 ^{vii}	0.88	1.98	2.833 (3)	163
N16—H16B...O15	0.88	1.95	2.611 (3)	131
N26—H26A...O14 ⁱ	0.88	2.15	2.987 (3)	159
N26—H26B...O25	0.88	1.97	2.628 (3)	130

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

Crystals of (I) are triclinic, and the space group $P\bar{1}$ was chosen and confirmed by subsequent analysis. H atoms bonded to C or N atoms were treated as riding atoms, with C—H distances of 0.98 Å and N—H distances of 0.88 Å. H atoms bonded to O atoms were located from difference maps and refined initially using DFIX constraints (SHELXL97; Sheldrick, 1997), with O—H distances of 0.90 (2) Å for atom O1 and 0.82 (2) Å for atoms O2 and O3, and finally as riding atoms with these distances. Although there are voids in the structure of $\sim 73 \text{ \AA}^3$ per unit cell, there is no evidence that any solvent molecules are present within the voids. Firstly, the only significant peaks in the difference map are clustered around the Ba atoms. In addition, the SQUEEZE option in PLATON (Spek, 2003) did not suggest that there was any significant electron density within the voids. Finally, when a supernumerary O atom was included in the void and refined with a fixed U_{iso} value, its site-occupancy factor refined to a value of 0.036 (6), which is consistent with the absence of significant additional solvent in the void.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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 that have provided computing facilities for this work. RLG and MLGS thank the Spanish Ministerio de Ciencia y Tecnología for financial support (grant No. 2000-1667).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1638). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- 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.
- Low, J. N., Arranz, P., Cobo, J., Fontecha, M. A., Godino, M. L., López, R., Cannon, D., Quesada, A. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 680–682.
- Low, J. N., Arranz, P., Cobo, J., Fontecha, M. A., Godino, M. L., López, R. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 534–537.
- Low, J. N., Arranz, P., Cuesta, R., Gutiérrez, M. D. & Glidewell, C. (2003). *Acta Cryst.* **C59**, m21–m24.
- Low, J. N., Cannon, D., Quesada, A., Marchal, A., Melguizo, M., Noguerras, M., Sánchez, A. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 604–607.
- Low, J. N., Lopéz, M. D., Arranz Mascarós, P., Cobo Domingo, J., Godino, M. L., Garzon, R., Gutiérrez, M. D., Melguizo, M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* **B56**, 882–892.
- Low, J. N., Moreno, J. M., Sánchez, A., Arranz Mascarós, P., Godino Salido, M. L., López Garzon, R., Cobo Domingo, J. & Glidewell, C. (2001). *Acta Cryst.* **B57**, 317–328.
- 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). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Starbuck, J., Norman, N. C. & Orpen, A. G. (1999). *New J. Chem.* **23**, 969–972.