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catena-Poly[[[{*N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinato-*O*}pentaaquastrontium]-*μ*-*N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinato-*O*:*O′*] monohydrate]: coordination polymer chains linked by hydrogen bonds into a three-dimensional framework

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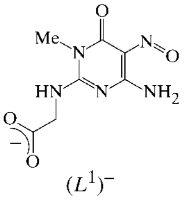
In the title compound, $[Sr(C_7H_8N_5O_4)_2(H_2O)_5]\cdot H_2O$, one of the anionic $(C_7H_8N_5O_4)^-$ ligands acts as a simple monodentate ligand coordinated *via* a carboxyl O atom, while the other acts as a bridging ligand between pairs of Sr atoms, utilizing one carboxyl O and the nitroso O atom, so generating a one-dimensional coordination polymer. Five water molecules are coordinated to Sr, resulting in eight-coordination in the form of a distorted square antiprism, while the sixth water molecule is hydrogen bonded to a coordinated water. The coordination polymer chains are reinforced by O—H···N and O—H···O hydrogen bonds and are linked into a three-dimensional framework by an extensive series of N—H···O and O—H···O hydrogen bonds.

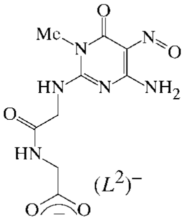
Comment

We have recently described and discussed the structures of a number of hydrated metal salts of the anions *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycinate, $(L^1)^-$, and *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)glycylglycinate, $(L^2)^-$ (Arranz Mascarós *et al.*, 1999, 2000; Low, Arranz, Cobo, Fontecha, Godino, López, Cannon *et al.*, 2001; Low, Arranz, Cobo, Fontecha, Godino, López & Glidewell, 2001; Low, Moreno Sánchez *et al.*, 2001). The simpler $(L^1)^-$ ligand can form simple hydrated salts, $[M(H_2O)_6](L^1)_2$, with no coordination of $(L^1)^-$ to the metal cation, as when $M^{2+} = Mg^{2+}$ or Zn^{2+} (Arranz Mascarós *et al.*, 1999, 2000); finite molecular aggregates $[Li(L^1)(H_2O)_3]$ and $[Mn(L^1)_2(H_2O)_4]\cdot 6H_2O$ are formed with Li^+ and Mn^{2+}, where the molecular aggregates are linked into three-dimensional frameworks by extensive hydrogen bonding (Low, Moreno Sánchez *et al.*, 2001); and with Na^+ and K^+, organic–inorganic hybrid sheets are formed, consisting of cations and anions only, which are then linked into three-dimensional frameworks by hydrogen bonds (Low, Moreno Sánchez *et al.*, 2001). The hydrated K^+ salt of $(L^2)^-$ takes the form of a three-dimensional coordination polymer, in whose construction the water molecules play no direct role (Low, Arranz, Cobo, Fontecha, Godino, López & Glidewell, 2001), while in $[Ca(L^2)_2(H_2O)_3]$, there are one-dimensional coordination polymer chains built from cations and anions only, linked by hydrogen bonds into a continuous framework (Low, Arranz, Cobo, Fontecha, Godino, López, Cannon *et al.*, 2001). Continuing with our structural study of the metal salts formed by $(L^1)^-$, we have now studied the hydrated Sr^{2+} salt.

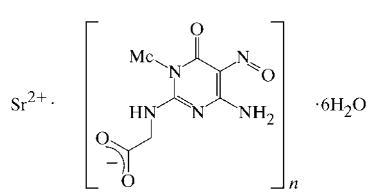
Although the composition of the Sr^{2+} derivative, (I), is identical to that of the Mg^{2+} analogue, $M(L^1)_2\cdot 6H_2O$, the constitution is entirely different. In particular, both anions in (I) are directly coordinated in a monodentate fashion to Sr *via* a carboxylate O atom, $[Sr(L^1)_2(H_2O)_5]\cdot H_2O$, whereas in the Mg salt, there is no coordination of the anions to the cation, thus $[Mg(H_2O)_6](L^1)_2$; one of the anions in (I) is also coordinated, *via* nitroso atom O25, to another Sr atom at the symmetry position $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$; the Sr coordination number is eight, as opposed to six in the Mg salt, but only five of the water molecules are directly bonded to Sr, while the sixth is hydrogen bonded to one of the coordinated water molecules (Fig. 1).



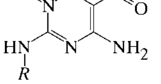
$(L^1)^-$



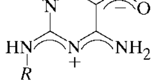
$(L^2)^-$



(I)



(*A*)



(*B*)

The range of Sr—O distances, 2.501 (2)–2.751 (2) Å, has an overall mean value of 2.618 (2) Å. However, within this range it is possible to distinguish three types of Sr—O interaction:

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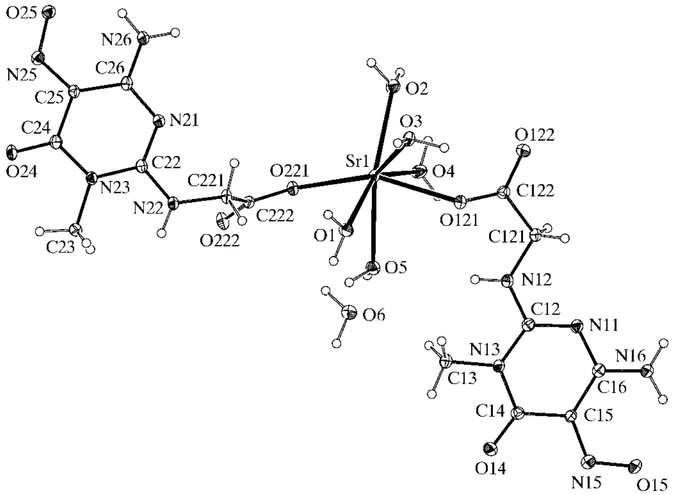

Figure 1
The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

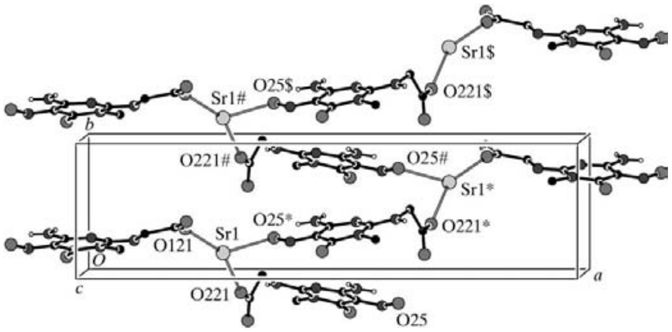

Figure 2
Part of the crystal structure of (I) showing the formation of a coordination polymer chain along [010]. For the sake of clarity, the water molecules and the H atoms bonded to C atoms have been omitted. The atoms marked with an asterisk (*), hash (#) or dollar sign ($) are at the symmetry positions $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(x, 1 + y, z)$ and $(1 - x, \frac{3}{2} + y, \frac{1}{2} - z)$, respectively.

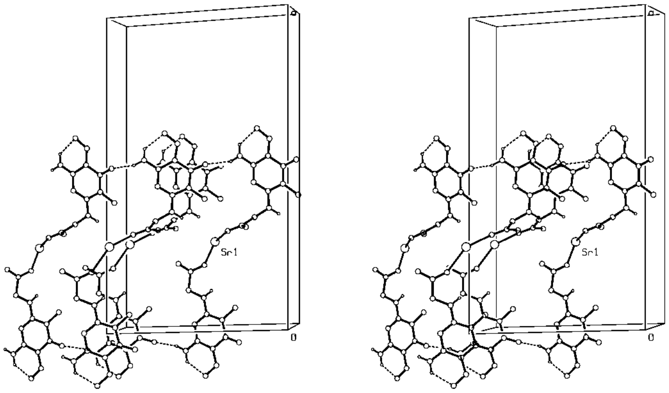

Figure 3
Stereoview of part of the crystal structure of (I) showing the formation of a hydrogen-bonded (100) sheet of $R_4^4(48)$ rings built from the ionic components only. For the sake of clarity, the water molecules and the H atoms bonded to C atoms have been omitted.

the bonds to carboxylate O have a mean value of 2.555 (2) Å, those to water O have a mean value of 2.616 (2) Å, while the unique bond to the nitrosyl O has a length of 2.751 (2) Å. This ordering of the different types is consistent with the variations observed in the hydrated Na^+ and K^+ salts of $(L^1)^-$ (Low, Moreno Sánchez *et al.*, 2001). In $[Ca(L^2)_2(H_2O)_3]$, the mean Ca—O distance is 2.420 (4) Å if all seven ligating O atoms are included, or 2.377 (4) Å if the outlier value for one weakly bound O atom is omitted. The differences between the mean Sr—O distance in (I) and the mean Ca—O distances in $[Ca(L^2)_2(H_2O)_3]$ are *ca* 0.20 Å if Ca is regarded as seven-coordinate and *ca* 0.24 Å if Ca is regarded as six-coordinate; these differences precisely reflect the differences between the corresponding ionic radii as tabulated by Shannon & Prewitt (1970), *i.e.* Ca^{2+} (seven-coordinate) 1.07 Å, Ca^{2+} (six-coordinate) 1.00 Å, and Sr^{2+} (eight-coordinate) 1.25 Å. The geometry of the SrO_8 polyhedron takes the form of a distorted square antiprism, typical of this coordination number.

The effect of the bridging action of one of the anions in (I) is the generation of a coordination polymer chain running parallel to the [010] direction, and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ (Fig. 2); a second, antiparallel, chain is generated by the 2_1 axis along $(\frac{1}{2}, -y, \frac{3}{4})$. It is striking that the formation of the coordination polymer involves only one of the two independent anionic ligands; in the one-dimensional coordination polymer formed by Ca^{2+} and the related anion $(L^2)^-$ (Low, Arranz, Cobo, Fontecha, Godino, López, Cannon *et al.*, 2001), the polymer chains lie across twofold rotation axes so that both anionic ligands participate in the chain formation. The formation of the one-dimensional chain polymers $[Sr(L^1)_2]_n$ and $[Ca(L^2)_2]_n$ may be contrasted with the formation of organic–inorganic hybrid sheets in the hydrated Na and K salts of $(L^1)^-$, in which the nitroso groups act as η^1 and η^2 ligands to Na and K, respectively (Low, Moreno Sánchez *et al.*, 2001).

As in $[Ca(L^2)_2]_n$, the coordination polymer chains in $[Sr(L^1)_2]_n$ are linked into a single three-dimensional framework by an extensive series of hydrogen bonds. In addition to the intramolecular N—H···O hydrogen bonds normally found in the anion (Low, Moreno Sánchez *et al.*, 2001) and the O5—H51*C*···O6 hydrogen bond to the sixth water molecule within the asymmetric unit, there are a total of 16 independent hydrogen bonds linking the neutral molecular aggregates; some of these reinforce the polymer chains and some link adjacent chains. There are two strictly planar three-centre O—H···O/N systems in which a water O—H moiety acts as the hydrogen-bond donor and the *ortho*-substituent atoms O*n*4 and N*n*5 (*n* = 1 or 2) act as the pair of acceptors (Table 2). In addition, there are 12 two-centre hydrogen bonds linking the molecular units, nine of O—H···O type and three of N—H···O type.

Water atom O1 acts as hydrogen-bond donor, *via* H11*C*, to O222^{iv} (symmetry operators are as defined in Table 2), and water O3 acts as donor, *via* H31*C* and H31*D*, to O221^{iv} and O4^{iv}, respectively; these three translational hydrogen bonds all reinforce the coordination polymer chain along [010]. Similarly, water atom O2 acts as donor, *via* H21*C*, to both O24^{v} and

N25^{v} in a three-centre hydrogen bond, which again reinforces the [010] chain by following the 2_1 axis along ($\frac{1}{2}$, y, $\frac{1}{4}$).

To analyse the linking of the coordination polymer chains, it is not, in fact, necessary to consider all of the inter-aggregate hydrogen bonds. Just three of the remaining hydrogen bonds, two of N—H···O type and one of the O—H···O hydrogen bonds, suffice to demonstrate the three-dimensional framework structure. Amino N16 in the type 1 anion (linked to Sr *via* O121) acts as hydrogen-bond donor, *via* H16*A*, to amido O14^{i}, so producing a $C(6)$ zigzag chain running parallel to [001] and generated by the glide plane at $y = \frac{1}{4}$; in an entirely similar manner, N26 in the type 2 anion (linked to Sr *via* O221) acts as hydrogen-bond donor, *via* H26*A*, to O24^{iii}, so producing a second $C(6)$ chain parallel to [001], this time generated by the glide plane at $y = -\frac{1}{4}$. The combination and propagation of these two simple chain motifs generates a deeply puckered sheet parallel to (100) in the form of a (4,4) net (Batten & Robson, 1998) built from a single type of $R_4^4(48)$ ring (Fig. 3). Two sheets of this type run through each unit cell and they are linked by the coordination polymer chain into bilayers comprising cations and anions. There are, of course, water molecules present which add considerable complexity to the overall hydrogen bonding; nonetheless it is possible to identify both one- and two-dimensional substructures (Figs. 2 and 3) built from the ionic components only.

The linking of the (100) bilayers into a continuous framework is most simply envisaged in terms of the formation of a [100] chain motif involving the ionic components together with just one of the water molecules, that containing O4. The cation–anion aggregates at (x, y, z) and ($1 - x$, $-y$, $1 - z$) are linked by that at (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$); N16 at (x, y, z) acts as hydrogen-bond donor to O14 at (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) (*cf.* Fig. 3), while O25 at ($1 - x$, $-y$, $1 - z$) is coordinated to the Sr at (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) (*cf.* Fig. 3). At the same time, the aggregates at ($1 - x$, $-y$, $1 - z$) and ($1 + x$, y, z) are linked by the O4 water molecule (Table 2); O4 at ($1 + x$, y, z), which is coordinated to the Sr at ($1 + x$, y, z), acts as hydrogen-bond donor, *via* H41*C*, to O15 at ($1 - x$, $-y$, $1 - z$), and O4 at ($1 - x$, $-y$, $1 - z$) similarly acts as donor to O15 at ($1 + x$, y, z), so generating a centrosymmetric $R_2^2(26)$ ring. In this way, the ionic aggregates at (x, y, z) and ($1 + x$, y, z) are linked *via* a $C_2^2(28)[R_2^2(26)]$ chain of rings, and hence all of the (100) bilayers are linked into a continuous framework.

Not only do the two anionic ligands in (I) exhibit different modes of coordination to Sr, but they adopt significantly different conformations (Table 1). In the type 1 anion, the torsion angles along the sequence of bonds from Sr1 to N11 can be classified as *ac, ap, ap, sp* (where *ap* denotes antiperiplanar, and so on), while the corresponding sequence of torsion angles in the type 2 anions is *sp, ap, ac, sp* (*cf.* Fig. 1).

Within the anionic ligands, the pattern of bond distances reproduces the pattern observed earlier, both in salts of $(L^1)^-$ (Low, Moreno Sánchez *et al.*, 2001) and in the neutral HL^1 (Low *et al.*, 2000), and point to the delocalized form (B) as more important than the classically localized form (A). We note, in particular, that the values of $\Delta\{\Delta = [d(\text{C—N}) - d(\text{N—O})]\}$ for the nitroso groups in the two independent anions are 0.060 (4) and 0.053 (4) Å, comfortably within the range previously observed in other metal salts of $(L^1)^-$, consistent with (B). In this connection, it is of interest to note that the O4—H41*C*···O15^{i} hydrogen bond [symmetry code: (i) $-x$, $-y$, $1 - z$], having the uncoordinated nitroso O atom as acceptor, has very short H···O and O···O distances (Table 2), characteristic of O—H···O hydrogen bonds having an anionic rather than a neutral O atom as acceptor and thus entirely consistent with the dominance of the polarized form (B). In the other anion, the nitroso O25 atom does not act as an acceptor of intermolecular hydrogen bonds as it is coordinated to Sr.

Experimental

Equimolar quantities of strontium chloride hexahydrate and of $(NH_4)(L^1)$ were separately dissolved in water. When the solutions were mixed, a pink crystalline precipitate of (I) was produced. Analysis, found: C 26.0, H 4.3, N 21.6%; $C_{14}H_{28}N_{10}O_{14}Sr$ requires: C 25.9, H 4.4, N 21.6%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$[Sr(C_7H_8N_5O_4)_2(H_2O)_5]\cdot H_2O$
$M_r = 648.08$
Monoclinic, $P2_1/c$
$a = 25.0078\ (8)$ Å
$b = 6.74160\ (10)$ Å
$c = 14.3677\ (4)$ Å
$\beta = 92.4950\ (10)^\circ$
$V = 2419.99\ (11)$ Å^3
$Z = 4$
$D_x = 1.779$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5162 reflections
$\theta = 3.0$–27.5°
$\mu = 2.32$ mm^{-1}
$T = 120\ (2)$ K
Block, pink
0.46 × 0.28 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.415$, $T_{\max} = 0.654$
10 993 measured reflections
5162 independent reflections
4318 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 27.5^\circ$
$h = -32 \rightarrow 32$
$k = -8 \rightarrow 5$
$l = -11 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 1.06$
5162 reflections
355 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2 + 1.7980P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0151 (7)

Table 1
Selected geometric parameters (Å, °).

Sr1—O121	2.501 (2)	Sr1—O221	2.608 (2)
Sr1—O1	2.566 (2)	Sr1—O4	2.617 (2)
Sr1—O2	2.582 (2)	Sr1—O3	2.710 (2)
Sr1—O5	2.604 (2)	Sr1—O25^{i}	2.751 (2)
N15—O15	1.284 (3)	N25—O25	1.282 (3)
C16—N16	1.314 (4)	C26—N26	1.310 (4)
N11—C12—N12—C121	−3.5 (4)	N21—C22—N22—C221	−0.9 (4)
C12—N12—C121—C122	−166.9 (2)	C22—N22—C221—C222	−90.3 (3)
N12—C121—C122—O121	1.0 (4)	N22—C221—C222—O221	168.3 (2)
C121—C122—O121—Sr1	−123.8 (3)	C221—C222—O221—Sr1	25.8 (4)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N16—H16*A*···O14$^{\rm i}$	0.88	1.96	2.814 (3)	164
N16—H16*B*···O15	0.88	1.97	2.610 (3)	129
N22—H22···O3$^{\rm ii}$	0.88	2.07	2.900 (3)	156
N26—H26*A*···O24$^{\rm iii}$	0.88	2.00	2.745 (3)	141
N26—H26*B*···O25	0.88	1.99	2.654 (3)	131
O1—H11*C*···O222$^{\rm iv}$	0.87	1.85	2.692 (3)	161
O1—H12*D*···O122$^{\rm ii}$	0.95	1.77	2.691 (3)	163
O2—H21*C*···O24$^{\rm v}$	0.93	2.54	3.431 (3)	161
O2—H21*C*···N25$^{\rm v}$	0.93	2.03	2.708 (3)	129
O2—H22*D*···O222$^{\rm iii}$	0.88	1.94	2.740 (3)	150
O3—H31*C*···O221$^{\rm iv}$	0.90	1.93	2.828 (3)	175
O3—H32*D*···O4$^{\rm iv}$	0.98	2.27	3.007 (3)	131
O4—H41*C*···O15$^{\rm vi}$	0.92	1.75	2.665 (3)	173
O4—H42*D*···O222$^{\rm iii}$	0.91	2.12	3.027 (3)	174
O5—H51*C*···O6	0.99	1.87	2.813 (3)	158
O5—H51*D*···O122$^{\rm ii}$	0.89	1.92	2.801 (3)	173
O6—H61*C*···O14$^{\rm vii}$	0.98	2.60	3.168 (3)	118
O6—H61*C*···N15$^{\rm vii}$	0.98	2.11	3.084 (3)	173
O6—H62*D*···O1$^{\rm viii}$	1.00	1.99	2.955 (3)	161

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

H atoms were treated as riding atoms, with C—H = 0.98 (CH_3) or 0.99 Å (CH_2), and N—H = 0.88 Å. Water molecules were handled *via DFIX* followed by *AFIX* (*SHELXL*97; Sheldrick, 1997). The Ba analogue appears to be isomorphous, with a = 24.8881 (8), b = 6.8332 (2), c = 14.6302 (3) Å, β = 93.5292 (9)° and V = 2483.27 (12) Å^3.

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, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England, using a Nonius KappaCCD diffractometer. 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: FR1349). Services for accessing these data are described at the back of the journal.

References

Arranz Mascarós, P., Cobo Domingo, J., Godino Salido, M., Gutiérrez Valero, M. D., López Garzón, R. & Low, J. N. (2000). *Acta Cryst.* C**56**, e4–e5.

Arranz Mascarós, P., Godino, M. L., López, R., Cuesta, R., Valenzuela Calahorro, C. & Martín Ramos, D. (1999). *Acta Cryst.* C**55**, 2049–2051.

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

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.* C**57**, 680–682.

Low, J. N., Arranz, P., Cobo, J., Fontecha, M. A., Godino, M. L., López, R. & Glidewell, C. (2001). *Acta Cryst.* C**57**, 534–537.

Low, J. N., López, M. D., Arranz Mascarós, P., Cobo Domingo, J., Godino, M. L., López Garzon, R., Gutiérrez, M. D., Melguizo, M., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 882–892.

Low, J. N., Moreno Sánchez, J. M., Arranz Mascarós, P., Godino Salido, M. L., López Garzon, R., Cobo Domingo, J. & Glidewell, C. (2001). *Acta Cryst.* B**57**, 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 & R. M. Sweet, pp. 307–326. London: Academic Press.

Shannon, R. D. & Prewitt, C. T. (1970). *Acta Cryst.* B**26**, 1046–1047.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (2001). *PLATON*. Version of July 2001. University of Utrecht, The Netherlands.