

An unusual  $P3_12$  framework for the  
 $\text{Ni}(4,4'\text{-bipyridine})(\text{H}_2\text{O})_4$  chainM. Enriqueta Díaz de Vivar,<sup>a\*</sup> Sergio Baggio,<sup>a</sup>  
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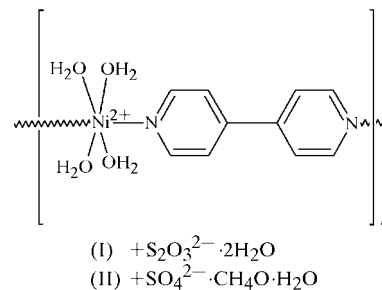
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*catena*-Poly[[[tetraaquanickel(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2N:N'$ ] thiosulfate dihydrate],  $\{[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}\}_n$ , (I), and *catena*-poly[[[tetraaquanickel(II)]- $\mu$ -4,4'-bipyridine- $\kappa^2N:N'$ ] sulfate methanol solvate monohydrate],  $\{[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{CH}_3\text{O} \cdot \text{H}_2\text{O}\}_n$ , (II), are built up of  $\{[\text{Ni}(4,4'\text{-bipy})(\text{H}_2\text{O})_4]^{2+}\}_n$  chains (4,4'-bipy is 4,4'-bipyridine) interwoven in an unusual  $P3_1$  fashion. Voids are filled by the corresponding counter-anions and solvate molecules, defining a complex three-dimensional network surrounding them. In both structures, the cationic chains evolve around a set of twofold axes passing through the  $\text{Ni}^{\text{II}}$  ions and bisecting the aromatic amines through their N (and their opposite C) atoms.

## Comment

In recent times, the possibility of inducing solid-state architectures with particular and predetermined structural properties has aroused great interest among structural chemists (Janiak, 2000; Qin *et al.*, 2005, and references therein). This interest has led to an extensive exploration of potential building units with binding peculiarities presumably leading to, or at least tending towards, certain expected final molecular assemblies. The entities explored have in general been monomers of diverse sizes and interaction capabilities, and only a few non-monomeric structures have been probed as directional building blocks. Among them, polymeric chains built up from a  $[\text{Tr}(\text{bipy})(\text{H}_2\text{O})_4]$  (Tr is a transition metal and bipy is 4,4'-bipyridine) elemental unit have proved to be versatile and efficient. A large number of structures having these chains as the building motif have been reported in the last few years. We could trace 55 entries (46 of them polymeric) in the Cambridge Structural Database (CSD; November 2005 release, plus updates; Allen, 2002), distributed among several cations (Co 19 cases, Mn 11, Zn eight, Cu and Ni seven each, Cd two and Fe one), covering a wide range of crystal systems and space-group symmetries.

In spite of this diversity, nearly all the reported structures share a common characteristic, which seems to be almost a distinctive hallmark of these one-dimensional 'bricks': they



generate final three-dimensional networks where the cationic chains are disposed parallel to each other in a single direction, the interchain distances ultimately being determined by the size and binding characteristics of the accompanying anionic guests. Thus, it is possible to find tight arrays where the separation between parallel chains (hereinafter  $\delta$ ) is small [*e.g.* CSD refcode RAJLUK (Xie *et al.*, 2004), Tr = Co, guest = phthalate,  $\delta \sim 5.8 \text{ \AA}$ ] or others where this figure can be more than twice as large [*e.g.* CSD refcode NATBAL (Carlucci *et al.*, 1997), Tr = Zn, guest = bis(trifluoromethanesulfonate),  $\delta \sim 12.6 \text{ \AA}$ ]. In any case, we could not trace structures where the nearest chain approach was smaller than  $\sim 5.8 \text{ \AA}$ .

In contrast with the characteristics referred to above, we present here two new members of this large family, *viz.*  $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , (I), and  $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ , (II), characterized by the chains lying in three different directions around a  $3_1$  axis, at  $120^\circ$  to each other, and giving rise to a different three-dimensional arrangement for both hosts and guests. To our knowledge, this unusual disposition has rarely been reported so far, a recent example being the nickel complex *catena*- $\mu_2$ -4,4'-bipyridyl-tetraaquanickel hemi(1,2,4,5-benzenetetracarboxylate) monohydrate, (III) (Wang *et al.* 2006), and then only in a pseudo- $3_1$  fashion.

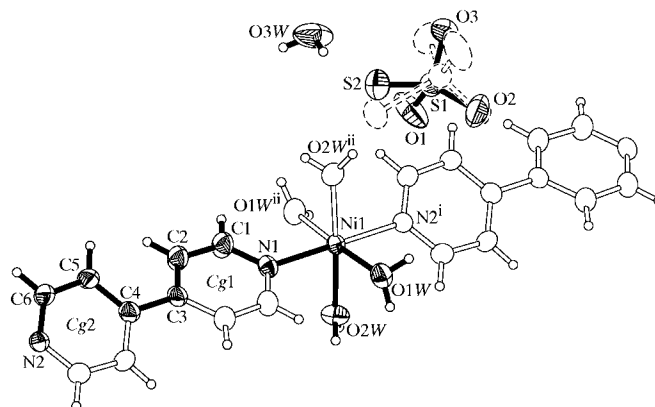


Figure 1

A diagram of (I), showing the atom- and chain-labelling schemes and the definitions of the centroids. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The independent part is drawn with full ellipsoids and the symmetry-related part with empty ellipsoids. Dashed lines indicate the disordered thiosulfate. (The symmetry codes are as in Table 1.)

Figs. 1 and 2 show schematic views of the single cationic motif in (I) and the two non-equivalent motifs in (II), respectively. The analogy is apparent: in both structures the cationic chains evolve around a set of twofold axes passing through the Ni<sup>II</sup> ions and bisecting the aromatic amines through their N (and their opposite C) atoms.

The cations appear surrounded by nearly perfect octahedral environments (Tables 1 and 2), defined by four water molecules in a planar arrangement and two apical N atoms from two translationally related bipy groups. All three independent bipy ligands depart significantly from planarity through the rotation of the pyridyl rings [24.8 (1)° in (II), and 43.1 (1) and 31.9 (1)° in (III)].

The thiosulfate group, acting as a counter-ion in (I), appears in a general position but is disordered into two overlapping half-occupancy symmetry-related images around a twofold axis. This results in a total of four complete S<sub>2</sub>O<sub>3</sub><sup>2-</sup> units in the unit cell, with their total negative charge balancing for the positive charge provided by the four ordered Ni<sup>II</sup> ions lying on special positions.

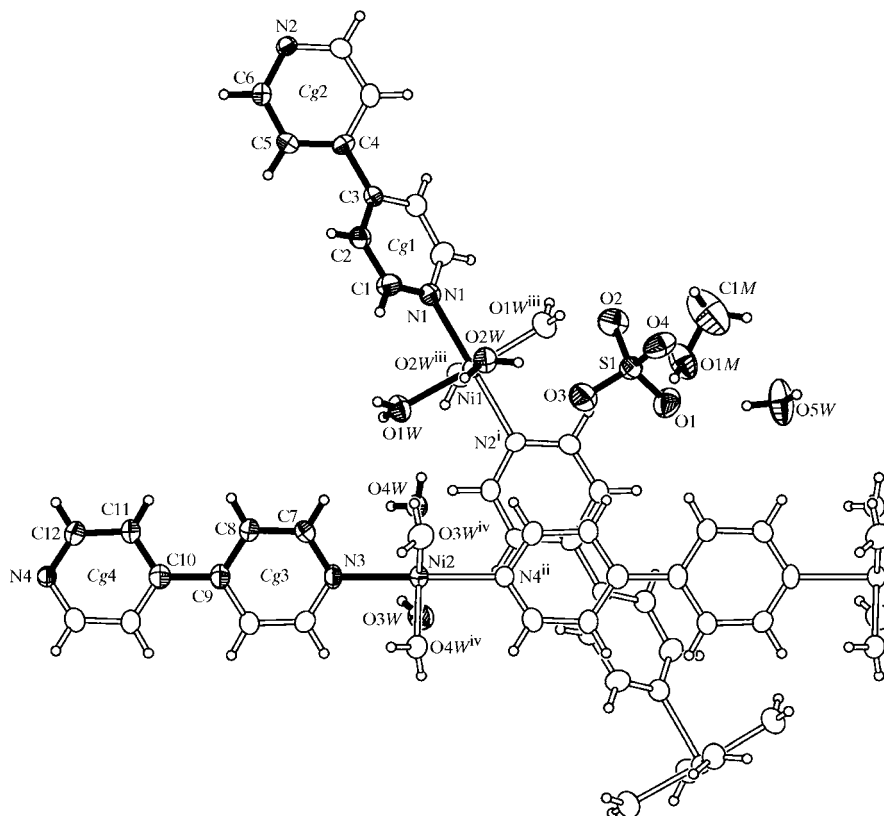
In the structure of (II), in contrast, the SO<sub>4</sub><sup>2-</sup> group appears to be ordered in a fully occupied general position site, in due correspondence with the two Ni<sup>II</sup> ions in special positions, thus also fulfilling its charge-balancing role.

Two water molecules in (I), and a water molecule and a methanol molecule in (II), provide stability to the structures, as shown below.

In spite of the fact that the compounds are not isostructural, the packing frameworks defined by the chain crossover are almost identical, as inspection of Figs. 3 and 4 confirms.

In the structure of (I), the single independent chain generates three different orientations, hereinafter referred to as *A*, *B* and *C* (Fig. 3), rotated by 120° from one another and shifted by  $c_{(I)}/3 = 3.7178(5) \text{ \AA}$  along the vertical axis, in an (*A*–*B*–*C*)(*A*–*B*–*C*) stacking sequence, where each pair of parentheses indicates a complete unit cell and each capital letter represents one definite chain orientation.

The case of (II) is slightly different. There are two independent Ni1 and Ni2 chains rotated from each other by exactly 120° and shifted along *c* by  $c_{(II)}/6 = 3.943(3) \text{ \AA}$ . By repeated application of the 3<sub>1</sub> symmetry operation, the latter pair generates six non-intersecting chains in the unit cell, the lower and upper half of the resulting cell being almost identical. In a similar description to that made above for (I), they would stack in an (*A*–*B*–*C*–*A'*–*B'*–*C'*)(*A*–*B*–*C*–*A'*–*B'*–*C'*) sequence, with the members of the *A/A'*, *B/B'* and *C/C'* pairs being strictly parallel to each other (Fig. 4) and shifted along the unique *c* axis by a similar amount to that found in (I) [ $c_{(II)}/2 = 11.830(3) \text{ \AA}$ , cf.  $c_{(I)} = 11.1523(13) \text{ \AA}$ ]. One of the most conspicuous differences between the two modes of stacking resides in the slight horizontal mismatch between members of each pair of parallel chains (*A/A'*, *B/B'* and *C/C'*; see Fig. 4), due to the fact that they are not symmetry related and are not even the same chains (*e.g.* *A* is an Ni1 chain, while



**Figure 2**

A diagram of (II), showing the atom- and chain-labelling schemes and the definitions of the centroids. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The independent part is drawn with full ellipsoids and the symmetry-related part with empty ellipsoids. (The symmetry codes are as in Table 2.)

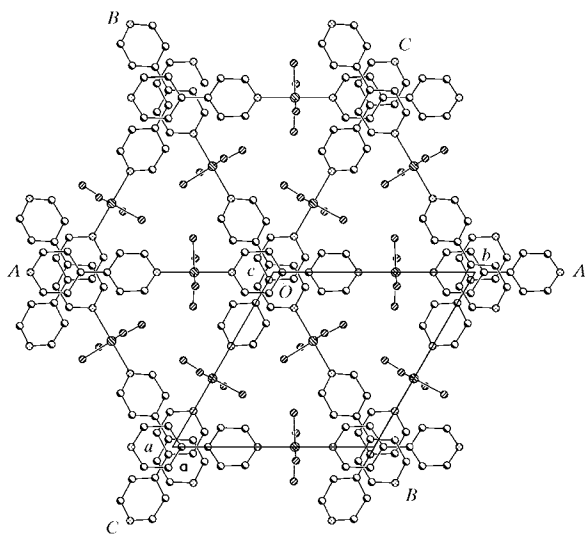
$A'$  is an Ni2 chain, etc.). The 'quasi' duplication of the unit cell along the  $c$  axis, as well as further similarities discussed in a first approximation, allow the description of the structure of (II) as a type of 'frustrated' supercell derived from (I). Even though it presents a different symmetry, the structure of (II) can be described in a similar manner (see below).

As in (I), the interchain separation in the basal plane of (II) is rather large [9.7785 (10) Å between chain axes], while that along  $c$  is much smaller, with a minimum interchain approach between consecutive members of  $c_{(II)}/6 = 3.943$  (1) Å. It is slightly larger than that in (I) [ $c_{(I)}/3 = 3.718$  (1) Å], but still significantly shorter than the smallest distances found in other packing patterns with a parallel arrangement of similar synthons ( $\delta \sim 5.8$  Å).

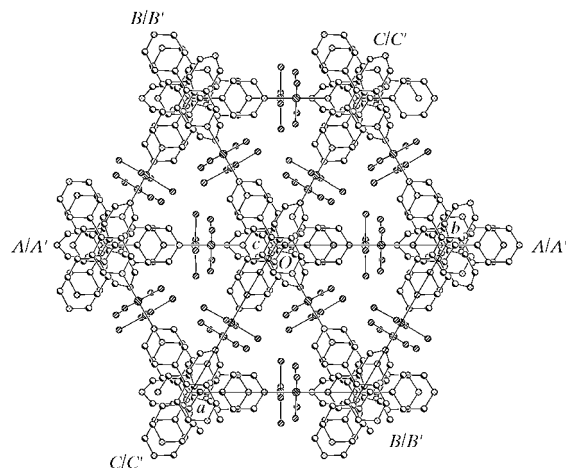
In (I), this short perpendicular approach between rings (Fig. 3) leads to some weak  $\pi$ - $\pi$  interactions along the unique axis [e.g.  $Cg1 \cdots Cg1(2 - y, 1 + x - y, \frac{1}{3} + z)$  or  $Cg1 \cdots Cg1(y, x, 2 - z)$ , with a centroid shift of 22.7 (1)°].

The fact that consecutive chains in (II) are not symmetry related appears to jeopardize the setting up of similar contacts, in spite of a seemingly similar overlap. Consecutive rings define mean dihedral angles of ca 20°, and the shortest  $Cg \cdots Cg$  distances are larger than 4.5 Å. This disposition, however, favours some strong C-H $\cdots$  $\pi$  interactions, e.g.  $C2-H2 \cdots Cg4(-1 + x, y, z)$  or  $(1 - x, 1 - x + y, \frac{1}{3} - z)$ , with a H $\cdots$ Cg separation of 2.79 (1) Å.

The monoclinic nickel analogue, (III), presents a rather similar three-dimensional arrangement, although the symmetry relationship is only approximate, and is only evidenced when the monoclinic structure is viewed down  $c$  as a pseudo-hexagonal axis. The two independent chains in the structure, defined by atoms Ni1 and Ni2, are disposed parallel to the (001) plane, subtending angles of 119.5, 119.5 and 121.5° to each other, while separated by 3.872 Å along  $c$  and following an (A-B-C-B)(A-B-C-B) sequence, displaying



**Figure 3**  
A projection of the structure of (I) along [001], with the thiosulfate anions and water solvent molecules omitted, showing in projection the  $3_1$  disposition of the chains.



**Figure 4**  
A projection of the structure of (II) down [001], with the sulfate anions and solvent molecules omitted, showing in projection the  $3_1$  disposition of the chains. Note the parallel quasi-superimposed chains, separated by  $c/2$  in height, after one apparent 'whole turn' of the screw.

only a local pseudo- $3_1$  (A-B-C) or  $3_2$  (C-B-A) symmetry at sites B (those bearing Ni1 chains).

In both (I) and (II), the anions and solvent molecules filling the gaps between chains are tightly linked to each other through hydrogen bonding, thus allowing an alternative description of the crystal packing. In fact, both structures can be thought of as being composed of a very dense anionic 'matrix' composed of these anions and solvent molecules, presenting three families of channels parallel to the basal plane and directed along the  $a$ ,  $b$  and  $ab$  directions, where the cationic chains are nested, being attached to those 'walls' through further hydrogen bonding.

## Experimental

Crystals of (I) were obtained by slow room-temperature diffusion of a methanol solution of 4,4'-bipyridine into an aqueous solution of sodium thiosulfate and nickel chloride (molar ratio 1:1:1). After three months of undisturbed diffusion, a crop of small needles growing from a common centre was obtained, from which samples suitable for X-ray diffraction could be extracted. Specimens of compound (II) were obtained by slow room-temperature diffusion of a methanol solution of 4,4'-bipyridine into an aqueous solution of nickel chloride ( $NiCl_2 \cdot 6H_2O$ ) and potassium pyrosulfite ( $K_2S_2O_5$ ) in a 1:1:2 molar ratio. After four months of undisturbed diffusion, an aggregate of badly shaped deep-green crystals was obtained, from which the specimen used for data collection was extracted. The appearance of  $SO_4$  in the final product was due to decomposition of the original oxoanion under ambient conditions.

## Compound (I)

### Crystal data

$[Ni(C_{10}H_8N_2)(H_2O)_4]S_2O_3 \cdot 2H_2O$	$Z = 3$
$M_r = 435.11$	Mo $K\alpha$ radiation
Hexagonal, $P3_121$	$\mu = 1.47 \text{ mm}^{-1}$
$a = 11.3363$ (9) Å	$T = 274$ (2) K
$c = 11.1523$ (13) Å	$0.18 \times 0.08 \times 0.06 \text{ mm}$
$V = 1241.2$ (2) Å <sup>3</sup>	

## Data collection

Bruker SMART CCD area-detector diffractometer	10484 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	1907 independent reflections
$T_{\min} = 0.78$ , $T_{\max} = 0.92$	1725 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{\text{max}} = 0.52 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.082$	$\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$
$S = 0.98$	Absolute structure: Flack (1983),
1907 reflections	with 760 Friedel pairs
153 parameters	Flack parameter: 0.02 (2)
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

Ni1—O1W	2.055 (2)	Ni1—N2 <sup>i</sup>	2.101 (3)
Ni1—O2W	2.082 (2)	Ni1—N1	2.129 (3)
O1W <sup>ii</sup> —Ni1—O1W	176.44 (13)	O1W—Ni1—N2 <sup>i</sup>	88.22 (6)
O2W—Ni1—O2W <sup>iii</sup>	176.68 (14)	O2W—Ni1—N2 <sup>i</sup>	91.66 (7)
N2 <sup>i</sup> —Ni1—N1	180.000	O1W—Ni1—N1	91.78 (6)
O1W <sup>ii</sup> —Ni1—O2W	91.43 (9)	O2W—Ni1—N1	88.34 (7)
O1W—Ni1—O2W	88.68 (9)		

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

## Compound (II)

### Crystal data

$[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{CH}_4\text{O} \cdot \text{H}_2\text{O}$	$V = 2612.5 (5) \text{ \AA}^3$
$M_r = 433.08$	$Z = 6$
Hexagonal, $P3_121$	Mo $K\alpha$ radiation
$a = 11.2916 (10) \text{ \AA}$	$\mu = 1.29 \text{ mm}^{-1}$
$c = 23.660 (3) \text{ \AA}$	$T = 273 (2) \text{ K}$
	$0.16 \times 0.12 \times 0.10 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	21995 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	3968 independent reflections
$T_{\min} = 0.82$ , $T_{\max} = 0.88$	2906 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.076$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	$\Delta\rho_{\text{max}} = 0.92 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.144$	$\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$
$S = 0.92$	Absolute structure: Flack (1983),
3968 reflections	with 1470 Friedel pairs
265 parameters	Flack parameter: 0.01 (3)
H atoms treated by a mixture of independent and constrained refinement	

H atoms attached to C atoms were placed in their calculated positions, with aromatic C—H = 0.93  $\text{\AA}$ , and allowed to ride. H atoms bound to O atoms were located in a difference Fourier synthesis and refined with restrained distances O—H = 0.85 (2)  $\text{\AA}$  and  $\text{H} \cdots \text{H} = 1.35 (5) \text{ \AA}$ ; for all H atoms,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ . The thiosulfate anion in (I) appears on a general position but on a twofold axis, at colliding distance from its symmetry-related counterpart. For that

**Table 2**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

Ni1—O2W	2.072 (4)	Ni2—O4W	2.049 (4)
Ni1—O1W	2.081 (4)	Ni2—O3W	2.064 (4)
Ni1—N1	2.103 (6)	Ni2—N4 <sup>ii</sup>	2.109 (6)
Ni1—N2 <sup>i</sup>	2.112 (6)	Ni2—N3	2.120 (6)
O2W <sup>iii</sup> —Ni1—O2W	179.2 (2)	O4W <sup>iv</sup> —Ni2—O4W	177.0 (2)
O2W—Ni1—O1W	93.01 (15)	O4W—Ni2—O3W	86.45 (16)
O1W—Ni1—O1W <sup>iii</sup>	178.0 (2)	O3W <sup>iv</sup> —Ni2—O3W	177.2 (2)
O2W—Ni1—N1	89.61 (11)	O4W—Ni2—N3	88.49 (11)
O1W—Ni1—N1	88.99 (12)	O3W—Ni2—N3	91.39 (12)
N1—Ni1—N2 <sup>i</sup>	180.0	N4 <sup>ii</sup> —Ni2—N3	180.000 (2)

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

reason it was modelled as being disordered over two half-occupancy sites, without any further restraints. This was in agreement with the requirements for charge balance (see *Comment*).

For both compounds, data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL-NT* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3057). Services for accessing these data are described at the back of the journal.

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