

Cadmium nitrate coordination polymers with substituted pyridazino[4,5-*d*]pyridazines

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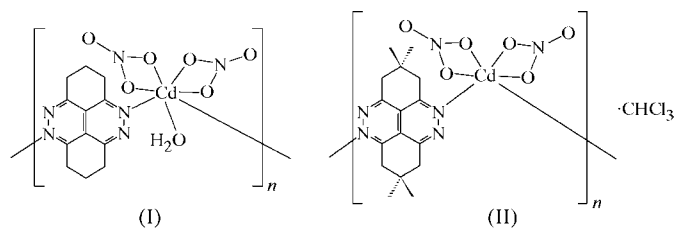
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catena-Poly[[aquabis(nitrato- κ^2O,O')cadmium(II)]- μ -1,2,3,6,7,8-hexahydrocinnolino[5,4,3-*cde*]cinnoline- $\kappa N^1:\kappa N^6$], [Cd(NO₃)₂(C₁₂H₁₂N₄)(H₂O)]_n, (I), and *catena*-poly[[[bis(nitrato- κ^2O,O')cadmium(II)]- μ -2,2,7,7-tetramethyl-1,2,3,6,7,8-hexahydrocinnolino[5,4,3-*cde*]cinnoline- $\kappa N^1:\kappa N^6$] chloroform solvate], [[Cd(NO₃)₂(C₁₂H₁₂N₄)]·CHCl₃]_n, (II), are the first structurally examined cadmium–pyridazine coordination compounds. They possess one-dimensional polymeric structures supported by the bidentate bridging function of the cinnolino[5,4,3-*cde*]cinnoline ligands, which lie about inversion centres. The Cd atoms are seven-coordinated in (I) and six-coordinated in (II), involving two bidentate nitrate groups [Cd–O = 2.229 (2)–2.657 (2) Å], two N atoms of the cinnoline ligands [Cd–N = 2.252 (2)–2.425 (2) Å], and, additionally, a water O atom in (I) [Cd–O = 2.284 (2) Å]. In (I), the coordinated organic and aqua ligands form an intramolecular O–H···N hydrogen bond [O···N = 2.730 (3) Å].

Comment

Open metal–organic topologies adopted around transition metal centres with bridging bidentate ligands provide attractive prototypes of porous lattices for application in the adsorption, separation and storage of gases (Janiak, 2003; Eddaoudi *et al.*, 2001). Unfortunately, most of these compounds exist as lattice clathrates and their framework structures are unstable, leading to the loss of the initially incorporated guest molecules. In part, this may be attributed to a lack of strong coordination interactions that support the connection of distal metal ions. Generation of open coordination lattices is feasible, employing polyfunctional ligands that provide multiple binding sites for coordination and/or hydrogen bonding, and recently there has been much attention given to this approach, with the use of polycarboxylates (Yaghi *et al.*, 2003), bipyrazoles (Rusanov, *et al.*, 2003) and other types of ligands. In this regard, condensed *N*-donor

aromatic heterocycles, and fused polycycles involving pyridazine, pyrimidine or pyrazine frames, are new and especially attractive classes of rigid multidentate ligands that could facilitate the connection of a set of metal ions, effective integration of the organic and inorganic counterparts, and formation of rigid coordination structures. In this context, we have prepared two cadmium–nitrate complexes, (I) and (II), with 1,2,3,6,7,8-hexahydrocinnolino[5,4,3-*cde*]cinnoline (*L*) and its 2,2,7,7-tetramethyl derivative (*Me₄L*), and report their structures here. Recently, we found that condensed pyridazino-pyridazines readily bind four copper(I) ions (Solntsev *et al.*, 2004) and these have application in the design of channelled frameworks.



Compounds (I) and (II) are the first structurally examined cadmium complexes with pyridazines. They adopt closely related one-dimensional polymeric structures that consist of zigzag coordination chains with a *trans*-bidentate function of the organic ligands (Figs. 1 and 2), compared with the bidentate bridging coordination of 4,4'-bipyridine and related ligands towards Cd^{II} ions (Barnett & Champness, 2003).

In the structure of (I), the coordination chains running along the *b* direction are bound by intermolecular hydrogen bonds [O···Oⁱⁱⁱ = 2.930 (2) Å; symmetry code: (iii) 1 + *x*, *y*, *z*] between the coordinated water molecules of one chain and the O atoms of the nitrate anions of another chain (Fig. 3). Such a combination of coordination and hydrogen bonds yields tightly packed layers parallel to the *ab* plane.

For complex (II), the introduction of methyl groups to the aliphatic linkage of the organic ligand does not influence the

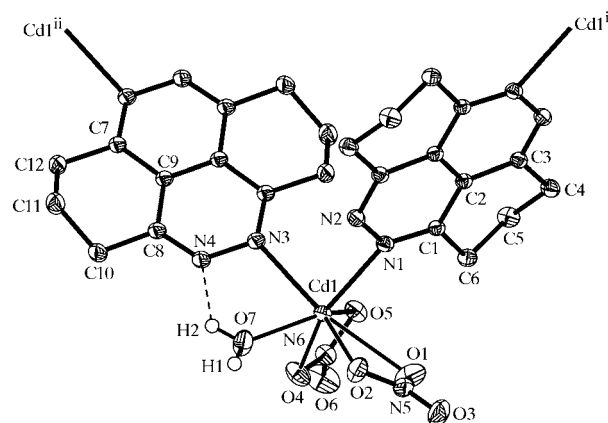


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound H atoms have been omitted and water H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the intramolecular hydrogen bond. [Symmetry codes: (i) $-x, 2 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]

coordination mode and topology of the polymer. However, the greater steric volume of the organic ligand effects the elimination of the water molecule from the coordination sphere of the Cd^{II} ion, which is decisive for the crystal packing. The shape-complementary situation of the coordination chains produces layers in the *bc* plane (Fig. 4). The guest chloroform molecules (one equivalent per metal atom) are located between the layers and form weak C—H...O hydrogen bonds with the O atom of the counter-anion [C...O = 3.329 (3) Å and C—H...O = 139.3 (2)°] (Fig. 2). Tight packing of the chains also leads to a set of forced van der Waals contacts between Cl and O atoms [Cl1...O3(2 - *x*, -*y*, 1 - *z*) 3.120 (3) Å and Cl2...O3(2 - *x*, *y* - ½, ½ - *z*) = 3.015 (3) Å]. These separations are noticeably short and are the shortest Cl...O contacts observed for chloroform molecules (Cambridge Structural Database, Version 5.26 of November 2004; Allen, 2002).

The Cd^{II} ions in complex (I) are seven-coordinate and the coordination environment consists of two N atoms of the organic ligands, four O atoms from two bidentate nitrate

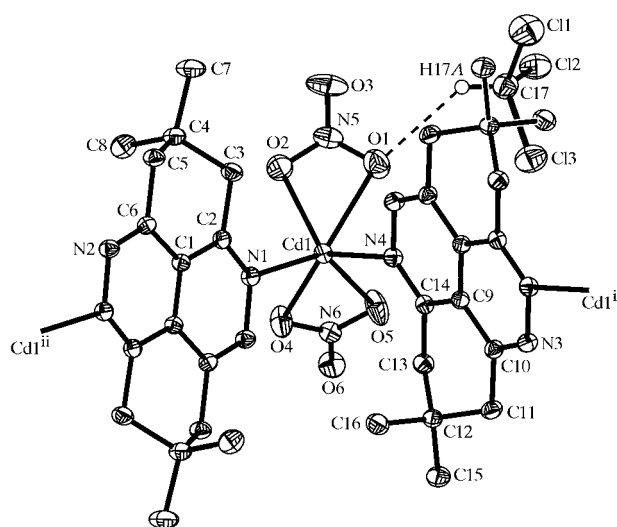


Figure 2

The structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level. The H atoms of the organic ligands have been omitted. The dashed line indicates the hydrogen bond to the chloroform molecule. [Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) 1 - *x*, -*y*, 1 - *z*.]

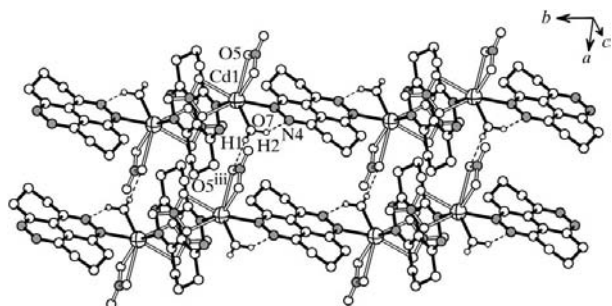


Figure 3

A perspective view of the structure of (I), showing the hydrogen bonding (dashed lines) between coordination zigzag chains. N atoms are shaded grey. [Symmetry code: (iii) 1 + *x*, *y*, *z*.]

groups and one coordinated water molecule (Fig. 1). In contrast, the Cd^{II} ions in complex (II) have a distorted octahedral environment involving two *cis* N atoms from the organic ligands and four O atoms of the bidentate nitrate groups (Fig. 2). This structure is the first example of a CdN₂O₄ six-coordinate Cd^{II} ion with two bidentate nitrate groups. For both compounds, the nitrate anions are coordinated in a typical unsymmetrical manner with two kinds of Cd—O bond lengths, namely Cd1—O2 and Cd1—O4 bonds [2.229 (2)–2.380 (2) Å], and longer Cd1—O1 and Cd—O5 bonds [2.384 (2)–2.657 (2) Å] (Tables 1 and 3). For complex (I), the Cd1—O7(water) bond length [2.284 (2) Å] appears to be even shorter than the Cd—O(nitrate) bond length [Cd—O = 2.302 (2)–2.657 (2) Å]. This is the shortest known Cd—O(water) coordination bond with this type of environment of the Cd^{II} ion; it may be compared with parameters of other aquanitratocadmium complexes with bis(2-pyridyl)acetylene [2.310 (1) Å; Zaman *et al.*, 2003] and quinoline [2.35 (2) Å; Cameron *et al.*, 1973]. Due to the higher coordination number of the central atom, the Cd—N bond distances for (I) [2.300 (2) and 2.425 (2) Å] are slightly longer than those for (II) [2.251 (2) and 2.307 (2) Å], while the Cd—N bonds are almost orthogonal in both structures [90.97 (6) and 87.73 (6)°].

In both structures, there are two independent ligand molecules, each of which displays inversion symmetry. The two unique ligand molecules in (I) are also chemically different, since only one of them forms strong intramolecular O—H...N hydrogen bonds with the two coordinated water molecules [O7...N4 = 2.730 (3) Å] (Figs. 1 and 3). This hydrogen bond is a new structural feature of metal-pyridazine complexes, although the possibility of effective interaction between adjacent pyridazine and water ligands may presumably be regarded as an important factor for the geometry of the

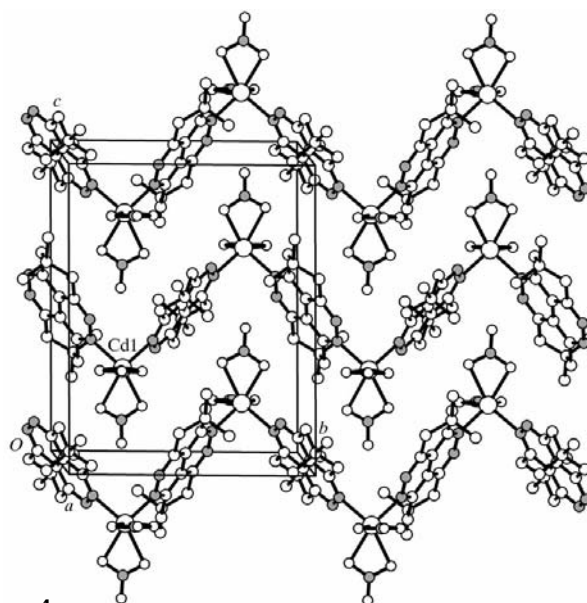


Figure 4

A perspective view of the structure of (II), showing the shape-complementary packing of the coordination zigzag chains. Chloroform solvent molecules and H atoms have been omitted.

coordination sphere and for the overall bulk structure. A comparable example of an intramolecular interaction between coordinated methyl and pyridazine ligands was reported for the Pt(CH₃)₃(pdz)₂Cl complex [N···C = 3.175 (10) Å and C—H···N = 121.5 (6)°; Abel *et al.*, 1994].

The geometry of the aromatic frame within molecules of ligands *L* [in (I)] and Me₄*L* [in (II)] is similar (Tables 1 and 3) and is comparable with the structure of unsubstituted pyridazino[4,5-*d*]pyridazine (Sabelli *et al.*, 1969). The N—N bonds [1.379 (2)–1.383 (2) Å] are longer, while the C—N bonds [1.310 (2)–1.320 (2) Å] are shorter than the corresponding parameters for the prototypic 1,2,4,5-tetrazine (C—N = 1.334 Å and N—N = 1.321 Å; Bertinotti *et al.*, 1956). In both structures, the pyridazine *d*-bonds [C—C = 1.369 (2)–1.381 (2) Å] are appreciably shortened with respect to pairs of *c*- and *e*-bonds [C—C = 1.416 (2)–1.425 (2) Å] and especially compared with the very long C9—C10 bond in 1,4,5,8-tetramethylnaphthalene (1.473 Å; Shiner *et al.*, 1984). Such alteration of the shorter and longer bonds within the aromatic frame reflects the large contribution of the bis-azine resonance structure (*e.g.* —C=N—N=C—). Indeed, condensed pyridazines readily undergo [4+2]-cycloadditions of the Diels–Alder type and behave as electron-poor bis-azadienes (Haider, 1991). Fused cyclohexane fragments of the ligands *L* and Me₄*L* adopt an ‘envelope’ conformation that is typical for six-membered cycles with three *sp*² atoms.

Thus, in the title cadmium nitrate complexes, the organic ligands *L* and Me₄*L* were coordinated to two metal ions and utilized only half of the available functionality, unlike complexes with copper(I) bromide and iodide (Solntsev *et al.*, 2004). This may be rationalized in terms of the stabilization of Cu^I–pyridazine coordination by back-bonding and may also be due to a significantly lower electrostatic repulsion of closely situated singly charged Cu^I ions bridged by pyridazine. The simple bidentate bridging function of the ligands towards Cd^{II} dications mitigates against the assembly of high-dimensional porous frameworks. Studies intended to resolve this problem with the use of unsubstituted condensed pyridazines and bipyridazines are in progress.

Experimental

The ligand 1,2,3,6,7,8-hexahydrocinnolino[5,4,3-*cde*]cinnoline (*L*) and its 2,2,7,7-tetramethyl derivative (Me₄*L*) were synthesized by the condensation of 1,3-cyclohexanedione (or 5,5-dimethyl-1,3-cyclohexanedione) and hydrazine, followed by air oxidation (Stille & Ertz, 1964). Compounds (I) and (II) were prepared using a common procedure described below. A solution of the ligand (0.1 mmol; *L*: 0.021 g; Me₄*L*: 0.027 g) in chloroform (1 ml) was added to a solution of cadmium nitrate tetrahydrate (0.034 g, 0.1 mmol) in methanol (1 ml). Propan-2-ol was added dropwise to the mixture until crystallization was observed and then methanol was added dropwise until the initially formed precipitate was totally dissolved. The solution was filtered and allowed to evaporate slowly. After 4–5 d, colourless prismatic crystals of the title complexes were filtered off, washed with propan-2-ol and dried in air; the yields were 50–60%. Different metal–ligand ratios in the solution did not affect the composition of the products.

Complex (I)

Crystal data

[Cd(NO₃)₂(C₁₂H₁₂N₄)(H₂O)]
M_r = 466.69
 Monoclinic, *P*2₁/*c*
a = 7.3240 (6) Å
b = 13.7493 (12) Å
c = 15.9016 (13) Å
 β = 90.720 (2)°
V = 1601.2 (2) Å³
Z = 4

D_x = 1.936 Mg m^{−3}
 Mo Kα radiation
 Cell parameters from 3796 reflections
 θ = 2.6–27.9°
 μ = 1.42 mm^{−1}
T = 223 (2) K
 Prism, colourless
 0.20 × 0.16 × 0.15 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.765, *T_{max}* = 0.816
 10135 measured reflections

3796 independent reflections
 3476 reflections with *I* > 2σ(*I*)
R_{int} = 0.015
 θ_{max} = 27.9°
h = −8 → 9
k = −18 → 17
l = −20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.022
wR(*F*²) = 0.056
S = 1.05
 3796 reflections
 236 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0279*P*)² + 0.9372*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.005
 Δρ_{max} = 0.54 e Å^{−3}
 Δρ_{min} = −0.39 e Å^{−3}
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.0108 (4)

Table 1

Selected geometric parameters (Å, °) for (I).

Cd1—O7	2.2841 (16)	N1—C1	1.318 (2)
Cd1—N1	2.3003 (15)	N1—N2	1.379 (2)
Cd1—O4	2.3017 (16)	N2—C3 ⁱ	1.314 (2)
Cd1—O2	2.3792 (16)	N3—C7 ⁱⁱ	1.320 (2)
Cd1—N3	2.4249 (15)	N3—N4	1.381 (2)
Cd1—O1	2.518 (2)	N4—C8	1.311 (2)
Cd1—O5	2.6471 (17)	C1—C2	1.425 (2)
O1—N5	1.251 (3)	C2—C2 ⁱ	1.376 (4)
O2—N5	1.259 (2)	C2—C3	1.423 (2)
O3—N5	1.222 (2)	C7—C9	1.425 (2)
O4—N6	1.263 (2)	C8—C9	1.424 (2)
O5—N6	1.254 (2)	C9—C9 ⁱⁱ	1.369 (4)
O6—N6	1.216 (2)		
O7—Cd1—N1	124.95 (7)	N1—Cd1—O1	83.40 (7)
O7—Cd1—O4	88.73 (7)	O4—Cd1—O1	82.42 (7)
N1—Cd1—O4	146.19 (6)	O2—Cd1—O1	51.59 (6)
O7—Cd1—O2	74.78 (6)	N3—Cd1—O1	159.29 (6)
N1—Cd1—O2	86.08 (6)	O7—Cd1—O5	135.65 (6)
O4—Cd1—O2	108.24 (7)	N1—Cd1—O5	96.13 (5)
O7—Cd1—N3	81.16 (5)	O4—Cd1—O5	50.95 (5)
N1—Cd1—N3	90.97 (6)	O2—Cd1—O5	129.57 (6)
O4—Cd1—N3	91.58 (6)	N3—Cd1—O5	82.31 (6)
O2—Cd1—N3	148.12 (6)	O1—Cd1—O5	78.52 (6)
O7—Cd1—O1	118.31 (6)		

Symmetry codes: (i) −*x*, −*y* + 2, −*z* + 1; (ii) −*x*, −*y* + 1, −*z* + 1.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<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>
O7—H1···O5 ⁱⁱⁱ	0.84	2.11	2.930 (2)	168
O7—H2···N4	0.89	2.05	2.730 (3)	133

Symmetry code: (iii) *x* + 1, *y*, *z*.

Complex (II)

Crystal data

[Cd(NO₃)₂(C₁₂H₁₂N₄)]·CHCl₃
M_r = 624.15
 Monoclinic, *P*2₁/*c*
a = 12.2570 (12) Å
b = 12.5085 (11) Å
c = 15.8471 (14) Å
 β = 102.687 (2)°
V = 2370.3 (4) Å³
Z = 4

D_x = 1.749 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5594 reflections
 θ = 2.4–27.9°
 μ = 1.31 mm⁻¹
T = 223 (2) K
 Prism, colourless
 0.22 × 0.17 × 0.15 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.762, *T_{max}* = 0.828
 13397 measured reflections

5594 independent reflections
 5130 reflections with *I* > 2σ(*I*)
R_{int} = 0.013
 θ_{max} = 27.9°
h = -8 → 16
k = -16 → 15
l = -20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.025
wR (*F*²) = 0.064
S = 1.06
 5594 reflections
 299 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 2.016P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.70 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.00154 (17)

Table 3

Selected geometric parameters (Å, °) for (II).

Cd1—N4	2.2515 (15)	N2—C6	1.316 (2)
Cd1—O2	2.2991 (18)	N3—C10	1.314 (2)
Cd1—N1	2.3074 (15)	N3—N4 ⁱⁱ	1.382 (2)
Cd1—O4	2.3394 (16)	N4—C14	1.310 (2)
Cd1—O5	2.3836 (18)	C1—C1 ⁱ	1.378 (3)
Cd1—O1	2.4307 (19)	C1—C2	1.418 (2)
O1—N5	1.248 (3)	C1—C6	1.423 (2)
O2—N5	1.268 (3)	C9—C9 ⁱⁱ	1.381 (3)
O3—N5	1.218 (3)	C9—C14	1.416 (2)
O4—N6	1.258 (2)	C9—C10	1.422 (3)
O5—N6	1.252 (2)	C17—Cl3	1.755 (3)
O6—N6	1.221 (2)	C17—Cl2	1.760 (3)
N1—C2	1.316 (2)	C17—Cl1	1.762 (3)
N1—N2 ⁱ	1.383 (2)		
N4—Cd1—O2	126.94 (7)	N1—Cd1—O5	136.42 (6)
N4—Cd1—N1	87.73 (6)	O4—Cd1—O5	53.49 (6)
O2—Cd1—N1	99.46 (6)	N4—Cd1—O1	86.46 (6)
N4—Cd1—O4	136.59 (7)	O2—Cd1—O1	53.60 (7)
O2—Cd1—O4	95.82 (7)	N1—Cd1—O1	137.53 (7)
N1—Cd1—O4	92.70 (6)	O4—Cd1—O1	119.40 (7)
N4—Cd1—O5	99.28 (6)	O5—Cd1—O1	86.00 (8)
O2—Cd1—O5	109.53 (8)		

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

All H atoms were located in difference maps and then refined as riding, with O—H distances constrained to 0.85 Å and C—H distances constrained to 0.96 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,O) for the methylene groups and the coordinated water molecule or 1.5*U*_{eq}(C) for the methyl groups.

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SMART-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.00; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1086). Services for accessing these data are described at the back of the journal.

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