Tetraaquabis(2,6-diamine-7H-purine-κN⁹)cobalt(II) benzene-1,2,4,5-tetra-carboxylate tetrahydrate

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The title compound, $[Co(C_5H_7N_6)_2(H_2O)_4](C_{10}H_2O_8)\cdot 4H_2O$, is an ionic structure comprising a $[Co(Hdap)_2(H_2O)_4]^{4+}$ cation (dap is 2,6-diaminopurine) in a general position, two benzene-1,2,4,5-tetracarboxylate (btc⁴⁻) anions straddling two different inversion centres and four solvent water molecules. The structure presents a remarkable degree of pseudosymmetry, with the Co^{II} cation lying almost exactly on a noncrystallographic pseudo-inversion centre. The overall spatial arrangement can be described in terms of cationic and anionic chains running along the [111] direction and linked into a three-dimensional network by a very complex hydrogen-bonding scheme in which all the available N—H and O—H groups take part.

Comment

2,6-Diaminopurine (hereinafter dap) is an attractive ligand which has not been explored extensively. Among its many interesting features are an impressive ability to participate in hydrogen bonding, acting as both a (multiple) donor and a (multiple) acceptor and thus giving rise to extremely complex hydrogen-bonding networks. In its Hdap⁺ protonated state, the group can display a special form of tautomerism known as prototropy, consisting of the relocation of the extra proton, which has the effect of forcing a rearrangement of the charge distribution. The different forms reported so far for the cation are shown in the first scheme, and the electron-density redistribution is evidenced by the different positions of the single and double bonds around the rings. The few known structures containing the Hdap⁺ cation (Cambridge Structural Database, Version 5.3; Allen, 2002) are $[M(Hdap)_2(hpt)_2(H_2O)_2]\cdot 4H_2O$ [H₂hpt is homophthalic acid; M is Ni^{II}, (IIa), or Co^{II}, (IIb); Atria, Corsini *et al.*, 2011], bis(Hdap) di-μ-croconato-$\kappa^3O,O':O'';\kappa^3O:O',O''$-bis[tetraaqua(croconato-κ^2O,O')neo-

dymium(III)], (III) (Atria, Morel *et al.*, 2011), and bis(Hdap)-(hpt)·7H₂O, (IV) (Atria *et al.*, 2010). All three Hdap⁺ groups appearing in (IIa), (IIb), (III) and (IV) are different, in

| Hdap⁺ in (IIa)/(IIb) | Hdap⁺ in (III) | Hdap⁺ in (IV) |
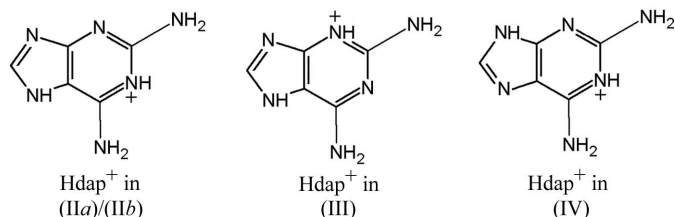
that protonation takes place at different N-atom sites. The group can also act as a ligand, though with rather restricted coordination capabilities. The molecule is capable of acting as a monocoordinated ligand linking the metal site through one of its lone imidazole N atoms, but this behaviour seems to be rather uncommon in dap chemistry: until very recently only one compound with the molecule binding to a metal centre appeared in the literature (Badura & Vahrenkamp, 2002), and only in the last year have we described compounds (IIa) and (IIb) as members of a new family of isomorphous compounds with the ligand acting in a similar N-monodentate fashion. Pursuing our interest in dap and Hdap⁺ structures, we present herein the title novel cobalt transition metal complex with the molecule acting as a charged singly protonated cation (Hdap⁺), binding the metal in an N-monodentate fashion, $[Co^{II}(Hdap)_2(H_2O)_4]btc\cdot 4H_2O$, (I), where H₄btc is benzene-1,2,4,5-tetracarboxylic acid.

(I)
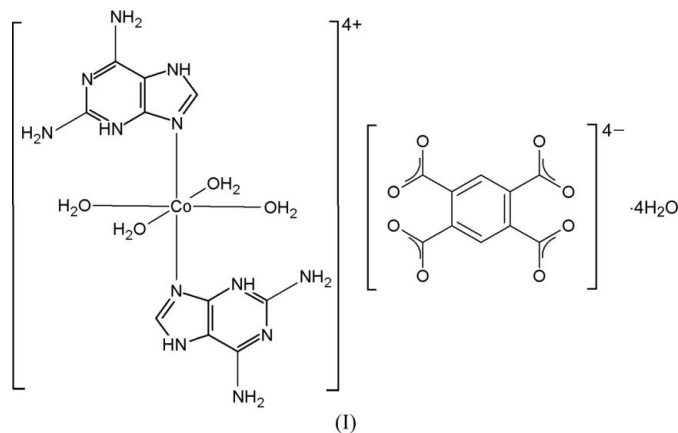
Compound (I) is an ionic structure comprising a $[Co(Hdap)_2(H_2O)_4]^{4+}$ cationic unit in a general position, charge-balanced by two btc⁴⁻ anions straddling two different inversion centres such that two independent half-anions in the asymmetric unit provide the required 4− charge. The asymmetric unit is completed by four solvent water molecules. The four aqua ligands bound to the Co^{II} centre (Fig. 1a) form a square-planar array defining the equatorial positions of an octahedron. The apical sites are occupied by slightly elongated bonds to two Hdap⁺ cations (discussed below), each coordinating *via* their single imidazole N-atom donor. The resulting octahedron is slightly elongated, with a mean value for the equatorial (shortest) Co—O bonds of 2.099 (6) Å, and an average of 2.146 (3) Å for the apical (longest) Co—N bonds.

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(a)

(b)
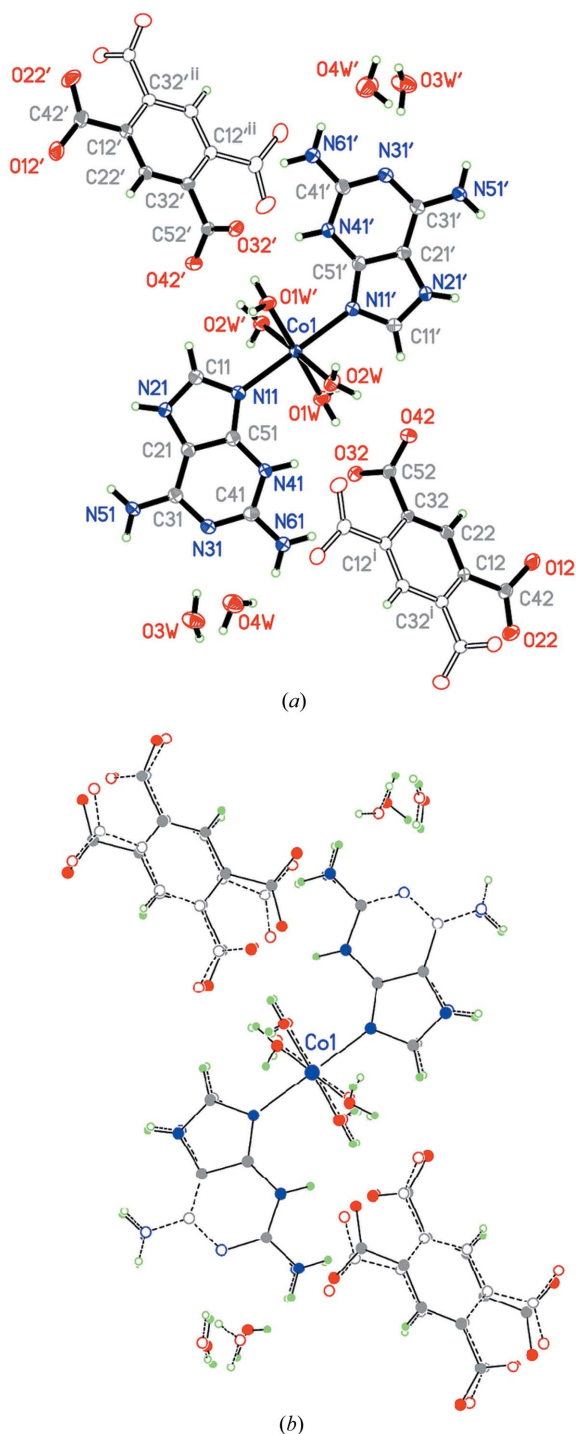
Figure 1
(*a*) The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, with independent atoms shown as heavy bonds and filled ellipsoids, and symmetry-related atoms shown as hollow bonds and empty ellipsoids. Primed atoms are related to unprimed ones by the 'pseudo inversion' at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. (*b*) Schematic overlap of the independent unit and its 'pseudo-inverted' counterpart. No least-squares fit was performed. [Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x - 1, -y + 1, -z$.]

Intramolecular bond angles at the metal centre span the narrow ranges 86.28 (4)–92.78 (4) and 175.21 (4)–178.53 (5)°. The structure presents a remarkable pseudosymmetry (pseudo-*I*-centring of the reported triclinic cell), with the Co^{II}

cation lying almost on a noncrystallographic $\bar{1}$ pseudo centre. To facilitate comparison, pseudosymmetrically related atoms have been labelled similarly (O1*W*, O1*W'*, *etc*).

Fig. 1(*b*) shows the overlap of the whole independent unit and its pseudosymmetry-related counterpart, without any least-squares fitting, and the correspondence is apparent [mean deviation of the fit is 0.22 (14) Å; see *Refinement* for details].

The centrosymmetric btc^{4-} units are very similar to each other and the four independent carboxylate groups present almost perfect delocalization [overall C—O range = 1.2451 (19)–1.2648 (19) Å]. The groups are, however, rotated around the C—C bond, possibly to minimize steric effects, and following the demands posed by the complex hydrogen-bonding scheme, with one of the COO$^-$ groups being almost parallel and the remaining one nearly orthogonal to the plane of the benzyl core [rotation angles = 4.9 (1)/4.0 (1) and 83.3 (1)/ 89.8 (1)° for the corresponding COO$^-$ groups in each anion].

Regarding the protonated Hdap$^+$ cation, to our knowledge the only reported structures containing the species are the above-mentioned compounds (II) to (IV), but none of them is strictly comparable with (I). The Hdap$^+$ cation in (III) bears the same proton disposition (see scheme), but in this structure the cation is not coordinated. On the other hand, Hdap$^+$ cations in (II*a*) and (II*b*) bear the same coordination behaviour but the protonation takes place at different sites (see scheme) and this has important consequences in the way in which both three-dimensional structures are built up. In (II*a*) and (II*b*), the extra H atom is located midway between the two amino groups (at N31), thus leaving the remaining atom (N41) free to make a strong intramolecular hydrogen bond accepting
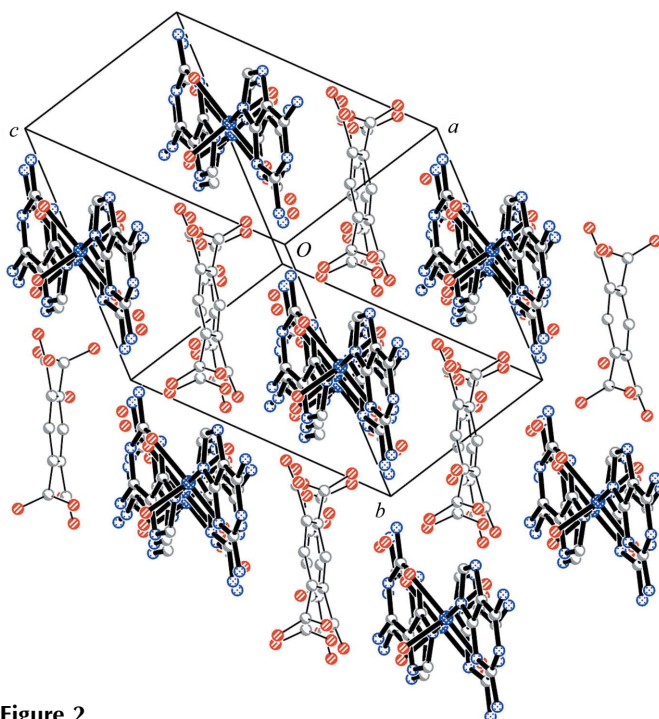
Figure 2
A packing view of (I), projected down the [111] direction of the cationic and anionic chains, which are therefore seen in projection. The former are shown in bold. H atoms have been omitted for clarity.
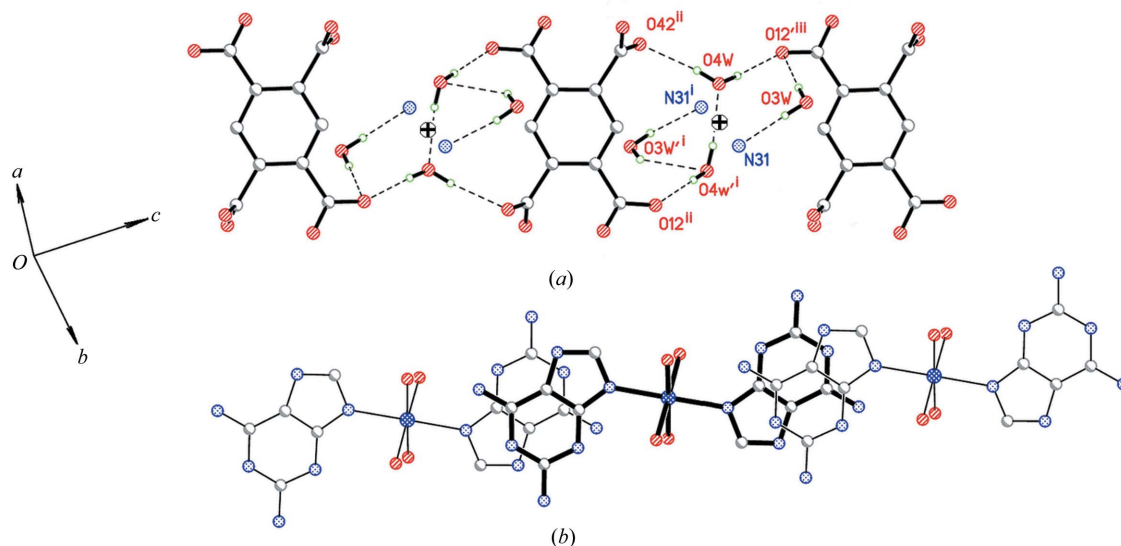
Figure 3
The chain formation in (I). (*a*) The anionic hydrogen-bonded chain, with embedded pseudo-inversion centres (shown as crossed circles). (*b*) The cationic chain formed by π–π interactions. [Symmetry codes: (i) $x, y, z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x, -y + 1, -z + 1$.]

one aqua H atom. In (I), in contrast, it is precisely atom N41 that is protonated, thus precluding this particular type of interaction but promoting, in turn, a stronger hydrogen-bonding link to the surrounding anions. As already suggested, intermolecular interactions are by far the most distinctive feature in these dap-containing structures. In the case of (I), there is an extremely large number of different possible donors (a total of 28, all of them involved in hydrogen bonding) and a comparable number of possible acceptors, as well as aromatic rings liable to be involved in π–π contacts. Table 2 shows the most important hydrogen bonds and Table 3 presents π–π interactions. The net result of their presence is a tightly bound three-dimensional structure, rather difficult to describe in the usual terms of a constructive process starting from strongly linked elemental bricks, further interlinked by weaker forces. However, inspection of Fig. 2 suggests one possible (though certainly not unique) description in terms of the interlinkage of cationic (heavy dark lines) and anionic (weaker lines) chains, running along the [111] direction and seen in projection in the figure. Figs. 3(*a*) and 3(*b*) give, in turn, individual views of each of these one-dimensional structures.

The anion/solvent water chain (Fig. 3*a*) is sustained internally by a network of hydrogen bonds involving solvent water molecules as donors and a mixture of water and btc^{4-} carboxylate O atoms as acceptors. The cationic chain (Fig. 3*b*) is, in turn, linked by π–π contacts between overlapping dap units, presented in detail in Table 3. This leaves 20 H atoms available for hydrogen bonding with the anion/solvent water chain, constituting the main factor in the assembly of the three-dimensional structure.

Experimental

2,6-Diaminopurine (0.300 g, 2 mmol) and cobalt acetate tetrahydrate (0.498 g, 2 mmol) were dissolved in water–ethanol (2:1 *v*/*v*, 10 ml) and the mixture was kept under reflux for 10 min. An aqueous solution

(40 ml) of benzene-1,2,4,5-tetracarboxylic acid (0.508 g, 2 mmol) and NaOH (0.080 g, 2 mmol) was added to this mixture, which was kept under reflux for another 4 h. Slow evaporation at room temperature for two weeks yielded single crystals of (I) suitable for X-ray diffraction.

Crystal data

[Co(C$_5$H$_7$N$_6$)$_2$(H$_2$O)$_4$](C$_{10}$H$_2$O$_8$)·4H$_2$O	β = 94.732 (1)°
M_r = 755.51	γ = 92.794 (1)°
Triclinic, $P\bar{1}$	V = 1409.84 (9) Å^3
a = 7.5730 (3) Å	Z = 2
b = 11.9386 (4) Å	Mo $K\alpha$ radiation
c = 15.6694 (6) Å	μ = 0.71 mm^{-1}
α = 91.026 (1)°	T = 150 K
	0.54 × 0.19 × 0.16 mm

Data collection

Bruker SMART CCD area-detector diffractometer	22822 measured reflections
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2002)	6235 independent reflections
	5525 reflections with $I > 2\sigma(I)$
T_{min} = 0.82, T_{max} = 0.89	R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	36 restraints
$wR(F^2)$ = 0.095	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.90 e Å^{-3}
6235 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
550 parameters	

Table 1
Selected bond lengths (Å).

Co1—O1*W*	2.1030 (10)	Co1—O2*W*′	2.1009 (11)
Co1—O1*W*′	2.1028 (10)	Co1—N11	2.1491 (12)
Co1—O2*W*	2.0910 (11)	Co1—N11′	2.1439 (12)

The amine groups exhibited slightly different geometries, as assessed by the deviations of the amine H atoms from the least-

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N21—H21$\cdots$O12^{i}	0.88	1.76	2.6235 (16)	166
N41—H41$\cdots$O32	0.88	1.91	2.7178 (16)	152
N51—H51$A\cdots$O42$'^{ii}$	0.87	2.17	2.9216 (16)	144
N51—H51$B\cdots$O22^{i}	0.87	1.94	2.8097 (16)	174
N61—H61$A\cdots$O4W	0.88	2.22	2.9832 (18)	145
N61—H61$B\cdots$O32	0.88	2.24	2.9984 (17)	144
O1W—H1$WA\cdots$O3W'^{iii}	0.85	1.90	2.7174 (16)	162
O1W—H1$WB\cdots$O32	0.85	1.87	2.7004 (15)	167
O2W—H2$WA\cdots$O42$'^{iv}$	0.85	2.04	2.8053 (16)	150
O2W—H2$WB\cdots$O42	0.85	2.00	2.8436 (15)	169
O3W—H3$WA\cdots$N31	0.85	2.05	2.8925 (17)	170
O3W—H3$WB\cdots$O12^{ii}	0.85	2.47	3.3132 (16)	172
O4W—H4$WA\cdots$O42^{v}	0.85	2.05	2.8723 (16)	162
O4W—H4$WB\cdots$O12^{ii}	0.85	1.95	2.7905 (16)	171
N21$'$—H21$'\cdots$O12$'^{vi}$	0.88	1.86	2.7007 (16)	159
N21$'$—H21$'\cdots$O22$'^{vi}$	0.88	2.54	3.2494 (17)	139
N41$'$—H41$'\cdots$O32$'$	0.88	1.91	2.7533 (16)	160
N51$'$—H51$C\cdots$O42^{vii}	0.86	2.28	2.9789 (16)	139
N51$'$—H51$D\cdots$O22$'^{vi}$	0.87	1.85	2.7256 (17)	176
N61$'$—H61$C\cdots$O4W'	0.87	2.16	2.9643 (18)	154
N61$'$—H61$D\cdots$O32$'$	0.88	2.43	3.1503 (17)	140
O1W'—H1$WC\cdots$O3W'^{viii}	0.85	1.92	2.7361 (16)	162
O1W'—H1$WD\cdots$O32$'$	0.85	1.86	2.7027 (15)	169
O2W'—H2$WC\cdots$O22^{v}	0.85	2.05	2.8569 (15)	157
O2W'—H2$WD\cdots$O42$'$	0.85	1.86	2.6952 (15)	168
O3W'—H3$WC\cdots$N31$'$	0.85	2.04	2.8864 (18)	173
O3W'—H3$WD\cdots$O4W'	0.85	2.31	2.9472 (18)	132
O4W'—H4$WC\cdots$O4W^{ix}	0.85	2.06	2.903 (2)	172
O4W'—H4$WD\cdots$O12^{vii}	0.85	1.95	2.7888 (17)	168

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

squares mean plane through the other atoms in the diaminopurine moieties: the C—NH$_2$ group at N51 is essentially planar, although slightly rotated around the C—N bond [with deviations of −0.15 (2) and 0.12 (2) Å from the mean plane]. In contrast, the other three amines exhibit different types and degrees of pyramidalization at the N atom. At N51$'$, only one H atom lies significantly out of the plane [deviations of 0.02 (2) and −0.10 (2) Å], while the deviations are greater at N61 [0.33 (2) and 0.24 (2) Å] and at N61$'$ [0.34 (2) and 0.23 (2) Å]. This varying degree of planarity for NH$_2$ groups is not uncommon for aromatic rings carrying two amino groups and might be due to the ability of the delocalized π-system of the ring to accommodate charge from one amino group, but not more (Linden, 2010).

The striking pseudo I-centring in the true primitive triclinic cell exhibited by structure (I) (see Fig. 1b) requires some additional description. The true unit cell is the primitive one reported herein, leading to a mean $I/\sigma(I)$ of 17.3 for all reflections and 9.1 for those with $h+k+l = 2n + 1$ (I-centring violations).

The pseudo-centring effect on the intensities does not arise (as it more typically does) from a heavy atom lying on a special position and the rest of the structure evolving more or less independently, but rather from a collective effect where all individual deviations from the pseudosymmetry are rather small. This can be seen both in Fig. 1(b) and, more quantitatively, in the small mean-square deviation of the separation of pseudo-related atoms and the (also small) s.u. value, i.e. 0.22 (14) Å. Finally, an independent structure resolution and refinement of the structure, using an 'I-centred cell' [viz. including the $(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z)$ symmetry operation] and the same data set, but purged of I-centring violations, could be performed without any substantial problems, converging perfectly acceptably, as can be seen from the following values for the 'I-centred' refinement

Table 3
π–π contacts (Å, °) for (I).

CCD is the centre-to-centre distance (distance between ring centroids), IPD is the mean interplanar distance (perpendicular distance from one plane to the neighbouring centroid) and SA is the mean slippage angle (angle subtended by the intercentroid vector to the plane normal); for details, see Janiak (2000). $Cg1$ is the centroid of the N11/C11/N21/C21/C51 ring, $Cg2$ is the centroid of the N11$'$/C11$'$/N21$'$/C21$'$/C51$'$ ring, $Cg3$ is the centroid of the N31/C31/C21/C51/N41/C41 ring and $Cg4$ is the centroid of the N311/C31$'$/C21$'$/C51$'$/N41$'$/C41$'$ ring.

Group 1/Group 2	CCD (Å)	SA (°)	IPD (Å)
$Cg1$–$Cg3^{viii}$	3.6196 (9)	24.4 (19)	3.29 (5)
$Cg2$–$Cg4^{iii}$	3.8769 (9)	29.6 (5)	3.37 (2)
$Cg3$–$Cg3^{viii}$	3.7438 (8)	30.03 (1)	3.241 (1)
$Cg4$–$Cg4^{iii}$	3.9125 (8)	31.72 (1)	3.328 (1)

Symmetry codes: (iii) $-x, -y, -z$; (viii) $1 - x, 1 - y, 1 - z$.

(the corresponding values for the true primitive cell are given in parentheses): $N_{total} = 11306$ (22822), $N_{unique} = 3112$ (6235), $N_{I>2\sigma(I)} = 2965$ (5525), $N_{parameters} = 255$ (506), $N_{restraints} = 12$ (24), $R_1 = 0.0370$ (0.0348), $wR_2 = 0.0992$ (0.0930), $S = 1.056$ (1.049).

The main difficulty found during the structure resolution in the 'centred' $I\bar{1}$ space group involved the location of the water H atoms, where those of O4W in particular appeared somewhat disordered. The reason for this is clearly seen in Figs. 1(b) and 3(a), where the positions of the 'pseudo-equivalent' atoms O4W and O4W' appear as the most conspicuous deviation from the pseudo-inversion symmetry, the pseudo-centres being shown as 'crossed circles' in Fig. 3(a).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Atria, A. M., Corsini, G., Herrera, N., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* C**67**, m169–m172.

Atria, A. M., Garland, M. T. & Baggio, R. (2010). *Acta Cryst.* C**66**, o547–o552.

Atria, A. M., Morel, M., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* C**67**, m17–m21.

Badura, D. & Vahrenkamp, V. (2002). *Inorg. Chem.* **41**, 6013–6019.

Bruker (2001). *SMART*. Version 5.624. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2002). *SAINT*. Version 6.22A (including *SADABS*). Bruker AXS Inc., Madison, Wisconsin, USA.

Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.

Linden, A. (2010). Private communication.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.