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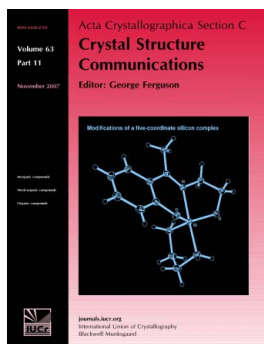
A polymeric cobalt(II) complex derived from citric acid (H₄cit) and 2,6-diaminopurine (dap): $\{[\text{Co}_4(\text{cit})_2(\text{dap})_4(\text{H}_2\text{O})_4] \cdot 6.35\text{H}_2\text{O}\}_n$

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A polymeric cobalt(II) complex derived from citric acid (H₄cit) and 2,6-diaminopurine (dap): $\{[\text{Co}_4(\text{cit})_2(\text{dap})_4(\text{H}_2\text{O})_4] \cdot 6.35\text{H}_2\text{O}\}_n$

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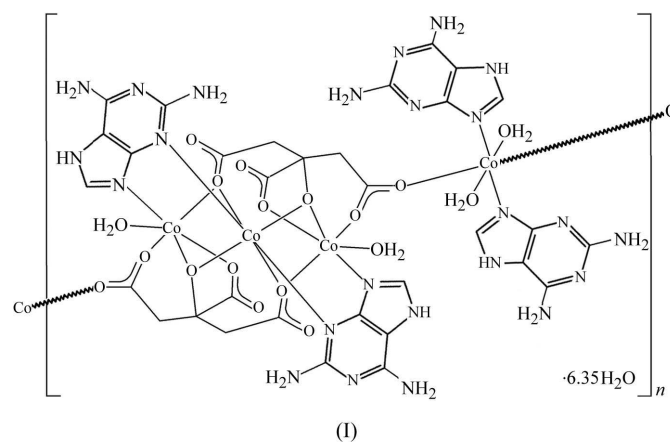
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Poly[[tetraaquad- μ_4 -citrato-tetrakis(2,6-diaminopurine)tetracobalt(II)] 6.35-hydrate], $\{[\text{Co}_4(\text{C}_6\text{H}_4\text{O}_7)_2(\text{C}_5\text{H}_6\text{N}_6)_4(\text{H}_2\text{O})_4] \cdot 6.35\text{H}_2\text{O}\}_n$, presents three different types of Co^{II} cations in the asymmetric unit, two of them lying on symmetry elements (one on an inversion centre and the other on a twofold axis). The main fragment is further composed of one fully deprotonated citrate (cit) tetraanion, two 2,6-diaminopurine (dap) molecules and two aqua ligands. The structure is completed by a mixture of fully occupied and disordered solvent water molecules. The two independent dap ligands are neutral and the cit tetraanion provides for charge balance, compensating the 4+ cationic charge. There are two well defined coordination geometries in the structure. The simplest is mononuclear, with the Co^{II} cation arranged in a regular centrosymmetric octahedral array, coordinated by two aqua ligands, two dap ligands and two O atoms from the β -carboxylate groups of the bridging cit tetraanions. The second, more complex, group is trinuclear, bisected by a twofold axis, with the metal centres coordinated by two cit tetraanions through their α - and β -carboxylate and α -hydroxy groups, and by two dap ligands bridging through one of their pyridine and one of their imidazole N atoms. The resulting coordination geometry around each metal centre is distorted octahedral. Both groups are linked alternately to each other, defining parallel chains along [201], laterally interleaved and well connected *via* hydrogen bonding to form a strongly coupled three-dimensional network. The compound presents a novel μ_4 - κ^5 O:O:O':O'',O''':O'''' mode of coordination of the cit tetraanion.

Comment

For some time, our group has focused attention on the study of the coordination chemistry of transition metal and lanthanide

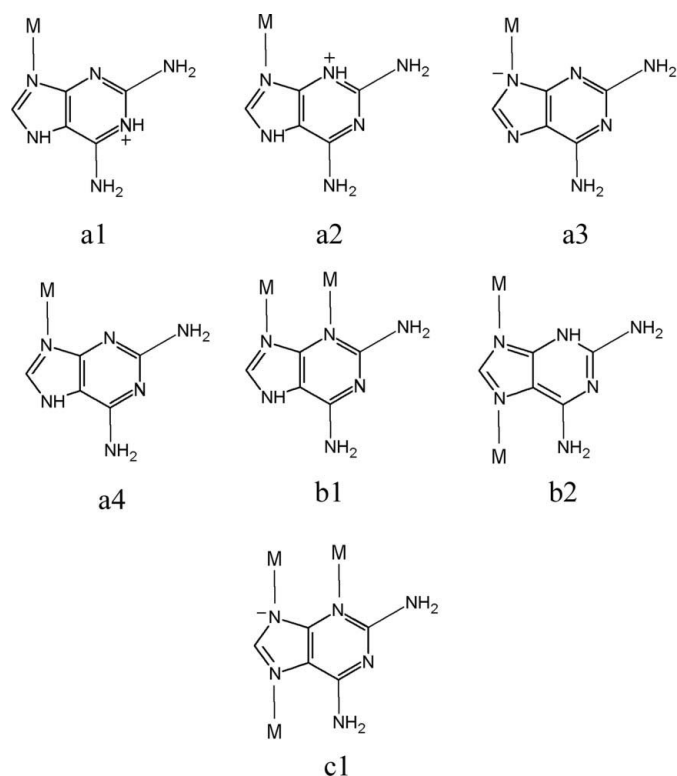
ions with (poly)carboxylic acids as ligands. An interesting candidate within this group is citric acid (H₄cit), not only due to its physiological importance [it is widely distributed in human plasma (Martin, 1986; Gautier-Luneau *et al.*, 2007) and participates in the catabolism of carbohydrates of aerobic organisms as a substrate in the tricarboxylic acid (or Krebs) cycle (Lippard & Berg, 1994)] but also for its intrinsic chemical interest. This molecule can give rise to mono- or multinuclear compounds of quite different natures through its binding to metal ions *via* an α -hydroxy, an α -carboxylate and/or one or both of its β -carboxylate groups (Matzapetakis *et al.*, 2001; Kefalas *et al.*, 2005; Zhou *et al.*, 2005). In addition, it can show various degrees of deprotonation, ranging from a neutral ligand to a tetraanion. A large number of complexes [about 360 in the Cambridge Structural Database (CSD), Version 5.33; Allen, 2002] have been reported, displaying coordination modes covering the range from μ_1 to μ_9 .



In parallel, in some of our previous research we found 2,6-diaminopurine (dap) to be an extremely versatile coligand but one that has not been adequately explored. Only ten complexes could be found in the CSD, in seven different binding modes (Fig. 1), with coordination numbers from μ_1 to μ_3 . Among the many interesting features of this ligand are its impressive ability to participate in hydrogen bonding, acting both as a (multiple) donor and a (multiple) acceptor and thus giving rise to complex hydrogen-bonding networks (see discussion below), and the fact that it can display a diversity of protonation states (+1, -1 or neutral). In any of these, the dap molecule may present prototropy, a special form of tautomerism consisting of a rearrangement of the charge distribution. This is illustrated in Fig. 1, where the electron-density redistribution is evidenced by the different positions of the single and double bonds around the rings.

Given all this, the possibility of having both ligands together in one compound seemed an extremely promising venture. Therefore, we synthesized the title Co^{II} complex, $\{[\text{Co}_4(\text{cit})_2(\text{dap})_4(\text{H}_2\text{O})_4] \cdot 6.35\text{H}_2\text{O}\}_n$, (I), and present its structure here.

Compound (I) crystallizes in the space group *C2/c* with three independent types of Co^{II} cations in the asymmetric unit, two of them lying on symmetry elements (Co1 on an

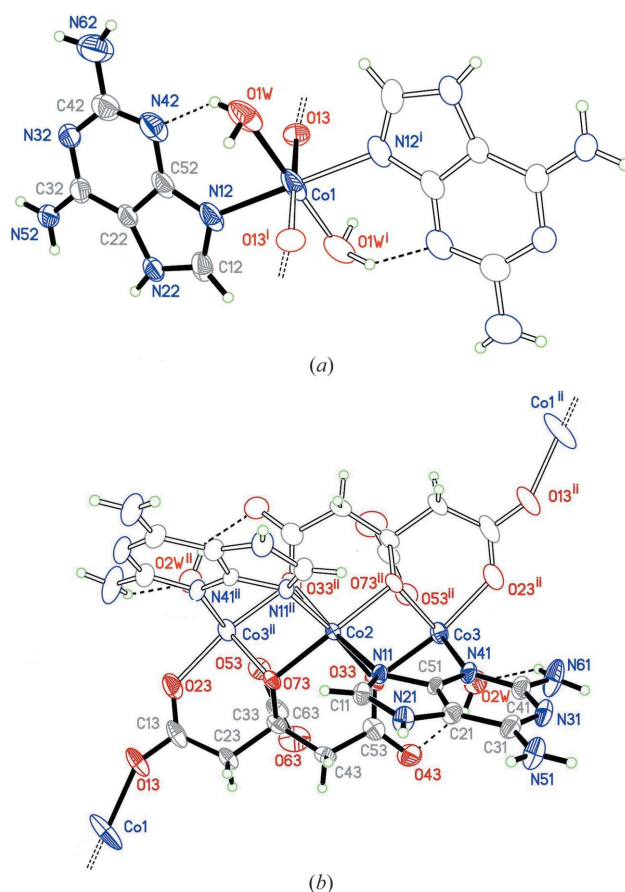

Figure 1

The different binding modes and protonation states of coordinated dap units in the literature, together with their CSD refcodes. μ_1 mode: a1 (OQUMOD, OQUMUJ and QUDLAD), a2 (QUDKQO and AWICUF), a3 (WULXEG) and a4 [title compound (I)]; μ_2 mode: b1 [QUDKAC and (I)] and b2 (QUDKIK and QUDKEG); μ_3 mode: c1 (QUDKUW). [References: OQUMOD and OQUMUJ (Atria, Corsini *et al.*, 2011); AWICUF (Atria, Garland *et al.*, 2011); QUDKAC, QUDKEG, QUDKIK, QUDKQO, QUDKUW and QUDLAD (Yang *et al.*, 2009); WULXEG (Badura & Vahrenkamp, 2002).]

inversion centre and Co2 on a twofold axis), while the third, Co3, is in a general position. The asymmetric unit content is completed by one fully deprotonated cit tetraanion, two dap ligands and two aqua ligands. The structure is completed by a mixture of fully occupied solvent water molecules (two in general positions and one on a twofold axis) and a disordered one, split over two positions.

There are two well defined coordination groups in the structure, one of them (mononuclear) containing only Co1 as its metal centre, and a second, trinuclear, one with Co2, Co3 and a symmetry-related congener of Co3. Fig. 2(a) presents the group containing Co1. The cation lies on a centre of symmetry and it is bound by one N atom from a mono-coordinated dap ligand, one O atom from one citrate tetraanion and one water ligand, plus their inversion-related counterparts. The octahedron thus defined is rather regular, with Co1–N/O distances in the range 2.055 (3)–2.143 (4) Å and central angles in the range 90 ± 3.36 (15)° (*cis*); *trans* angles are fixed by symmetry at 180°.

The Co2–Co3 group is more complex (Fig. 2b). Atom Co2 lies on a twofold axis, while atom Co3 occupies a general position. These three vicinal Co centres are multiply bridged by a cit tetraanion and a neutral dap ligand and their


Figure 2

Separate views of (a) the Co1 group and (b) the Co2–Co3 group of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 2, y, -z + \frac{3}{2}$.]

symmetry-related counterparts. The result is that both Co2 and Co3 end up with distorted octahedral environments, with Co–N/O distances in the ranges 2.030 (3)–2.184 (3) and 2.028 (3)–2.162 (4) Å, respectively, and central angles in the ranges 90 ± 13.26 (12) and 160.68 (16)– 173.39 (12)° for Co2 and 90 ± 8.88 (12) and 170.09 (13)– 173.90 (13)° for Co3.

The two independent dap ligands are neutral and participate in both the Co1 coordination group (dap2, in μ_1 mode, denoted a4 in Fig. 1) and the Co2–Co3 coordination environment (dap1, in N,N' - μ_2 mode, denoted b1 in Fig. 1). Both dap ligands present the same protonated N atom (N21 and N22) and thus the same prototropic state.

The cit tetraanions provide for charge balance, compensating the 4+ cationic charge of the four Co^{2+} cations. This 4– charge comes from the unprotonated α -hydroxy, α -carboxylate and both β -carboxylate groups. The ligand bridges four different Co^{II} cations through two bicoordinated and three monocoordinated O atoms. The resulting $\mu_4\text{-}\kappa^5\text{O}:\text{O}:\text{O}'\text{:}\text{O}'\text{:}\text{O}''\text{:}\text{O}'''\text{:}\text{O}''''$ mode seems to be novel for this ligand, as revealed by a search of the CSD. This binding behaviour mediates the cohesion of the Co2–Co3 group and at the same time provides a linkage between both groups to define chains running parallel to [201] (Fig. 3).

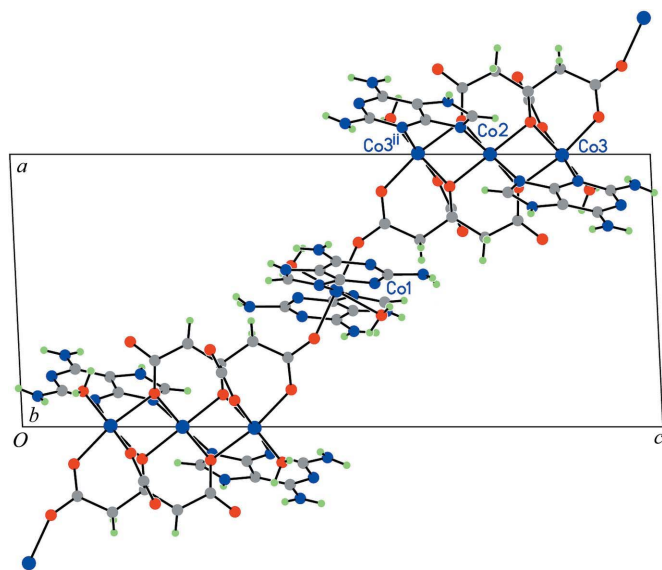


Figure 3
A projection of the structure of (I) along *b*, showing the [201] chain. See Fig. 2 for symmetry code.

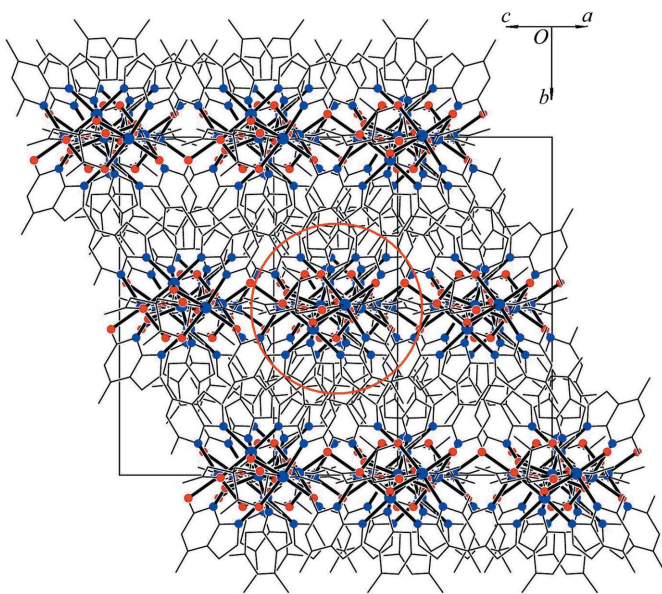


Figure 4
A packing view of (I) along [201], *i.e.* along the chains (shown in projection, heavy lines). The central circle highlights an isolated chain.

Neighbouring chains are laterally interleaved and well connected *via* hydrogen bonding. Fig. 4 presents a view down [201], showing the hydrophilic parts of the structure (in bold) approaching each other normal to the *b* direction, while the hydrophobic parts (lighter lines) form a kind of buffer, separating the former along *b*. The hydrogen-bonding contacts are almost impossible to represent in the projection shown, due to the heavy overlap, but are fully detailed in Table 1. The first four entries correspond to 'intrachain' bonds, shown in Figs. 2(*a*) and 2(*b*), and they determine *R*(6) rings (Bernstein *et al.*, 1995). The remaining hydrogen bonds serve to inter-

connect the chains in all directions perpendicular to the chains, to form a strongly coupled three-dimensional network.

The individual involvement in the hydrogen bonding of each ligand type (taking into account only the well determined water molecules) is as follows, in a donor/acceptor sequence: dap 8/5, cit 0/5 and water 7/5. It is apparent from these figures that the neutral dap ligand plays a significant role in the stabilization of the structure.

Experimental

To an aqueous solution (60 ml) containing citric acid (1 mmol, 0.192 g) and sodium hydroxide (4 mmol, 0.160 g) was added a mixture of 2,6-diaminopurine (2 mmol, 0.300 g) and cobalt acetate tetrahydrate (2 mmol, 0.498 g). The resulting mixture was heated under reflux for 4 h and then filtered. The filtrate was allowed to stand at room temperature for three weeks to give crystals of (I) suitable for X-ray analysis.

Crystal data

$[\text{Co}_4(\text{C}_6\text{H}_4\text{O}_7)_2(\text{C}_5\text{H}_6\text{N}_6)_4(\text{H}_2\text{O})_4] \cdot 6.35\text{H}_2\text{O}$	$\beta = 92.687 (5)^\circ$
$M_r = 1398.78$	$V = 4877.5 (19) \text{ \AA}^3$
Monoclinic, $C2/c$	$Z = 4$
$a = 10.548 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 18.669 (4) \text{ \AA}$	$\mu = 1.45 \text{ mm}^{-1}$
$c = 24.795 (6) \text{ \AA}$	$T = 150 \text{ K}$
	$0.18 \times 0.15 \times 0.14 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	20231 measured reflections
Absorption correction: multi-scan (SADABS in SAINT-NT; Bruker, 2002)	5466 independent reflections
$T_{\min} = 0.77, T_{\max} = 0.82$	4889 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.122$	$\Delta\rho_{\text{max}} = 1.05 \text{ e \AA}^{-3}$
$S = 1.27$	$\Delta\rho_{\text{min}} = -1.43 \text{ e \AA}^{-3}$
5466 reflections	
448 parameters	
26 restraints	

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O1 <i>W</i> —H1 <i>WA</i> ···N42	0.85 (1)	2.06 (4)	2.766 (6)	140 (6)
O2 <i>W</i> —H2 <i>WA</i> ···O43	0.85 (1)	2.04 (3)	2.773 (5)	144 (4)
N61—H61 <i>B</i> ···O2 <i>W</i>	0.84 (1)	2.32 (4)	3.017 (6)	140 (5)
O4 <i>W</i> —H4 <i>W</i> ···O53	0.85 (1)	2.09 (6)	2.835 (5)	147 (10)
O1 <i>W</i> —H1 <i>WB</i> ···N61 ⁱ	0.85 (1)	2.47 (2)	3.286 (7)	163 (4)
O2 <i>W</i> —H2 <i>WB</i> ···N32 ⁱⁱ	0.85 (1)	1.96 (1)	2.804 (5)	175 (5)
O3 <i>W</i> —H3 <i>WA</i> ···O73 ⁱⁱⁱ	0.85 (1)	1.94 (1)	2.778 (4)	168 (5)
O3 <i>W</i> —H3 <i>WB</i> ···N62 ⁱⁱⁱ	0.85 (1)	2.20 (2)	3.030 (8)	166 (5)
N21—H21···O63 ^{iv}	0.85 (1)	1.78 (2)	2.607 (5)	162 (5)
N51—H51 <i>A</i> ···N31 ^v	0.85 (1)	2.31 (1)	3.149 (5)	171 (5)
N61—H61 <i>A</i> ···O23 ^{vi}	0.84 (1)	2.20 (4)	2.842 (5)	133 (5)
N22—H22···O3 <i>W</i> ^{vii}	0.85 (1)	2.05 (2)	2.889 (6)	168 (6)
N52—H52 <i>B</i> ···O3 <i>W</i> ^{vii}	0.85 (1)	2.11 (2)	2.934 (6)	163 (5)
N62—H62 <i>A</i> ···O6 <i>W</i> ^w	0.85 (1)	2.07 (4)	2.834 (16)	149 (6)
N62—H62 <i>A</i> ···O6 <i>W</i> ^{w'}	0.85 (1)	2.05 (3)	2.85 (2)	157 (6)

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

Some solvent water molecules presented problems during the refinement: one (O6W) appeared split over two positions with depleted occupancy [$O6W' = 0.392$ (13) and $O6W'' = 0.273$ (14)], and its H atoms, as well as those for O5W, could not be found in the difference map and were not included in the final model.

The remaining H atoms were originally found in the difference Fourier map but were treated differently in the refinement. C-bound H atoms were repositioned in their expected positions and thereafter allowed to ride, with aromatic C–H = 0.93 Å and methylene C–H = 0.97 Å, while N- and O-bound H atoms were refined with restrained distances of N–H = O–H = 0.85 (1) Å and H...H = 1.35 (2) Å. One of the water H atoms (H1WB) required an antibumping restraint to prevent an unrealistic approach to atom Co1. In all cases, $U_{iso}(H) = 1.2U_{eq}(host)$.

In the final difference map, the maximum and minimum $\Delta\rho$ peaks are 1.05 and $-1.43 \text{ e } \text{Å}^{-3}$, respectively, at 0.49 and 1.02 Å from atom Co1. The rather complex character of the structure prevented some of the N-bound H atoms (H51B, H61B, H52A and H62B) from being involved in hydrogen bonding. In addition, it is worth noting that the space group should be considered centrosymmetric only on average; data reduction in the space group *C2/c* showed many small violations to the *c*-glide condition, while refinement in the space group *C2* did not improve the results yet doubled the number of parameters needed in the description of the structure. This may be partially responsible for the rather unusual weighting scheme needed to optimize the refinement.

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).

The authors acknowledge the Spanish Research Council (CSIC) for providing a free-of-charge licence to the CSD system (Allen, 2002). We are also grateful for funding by project Fondecyt 1120125.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3122). Services for accessing these data are described at the back of the journal.

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supplementary materials

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A polymeric cobalt(II) complex derived from citric acid (H₄cit) and 2,6-diaminopurine (dap): {[Co₄(cit)₂(dap)₄(H₂O)₄]·6.35H₂O}_n

Ana María Atria, José Parada, Maria Teresa Garland and Ricardo Baggio

Poly[[tetraaquadi-μ₄-citrato-tetrakis(2,6-diaminopurine)tetracobalt(II)] 6.35-hydrate]

Crystal data

[Co₄(C₆H₄O₇)₂(C₅H₆N₆)₄(H₂O)₄]·6.35H₂O
M_r = 1398.78
 Monoclinic, C2/c
 Hall symbol: -C 2yc
a = 10.548 (2) Å
b = 18.669 (4) Å
c = 24.795 (6) Å
 β = 92.687 (5)°
V = 4877.5 (19) Å³
Z = 4

F(000) = 2862
D_x = 1.905 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 10568 reflections
 θ = 1.9–26.1°
 μ = 1.45 mm⁻¹
T = 150 K
 Block, pink
 0.18 × 0.15 × 0.14 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 CCD rotation images, thin slices scans
 Absorption correction: multi-scan
 (SADABS in SAINT-NT; Bruker, 2002)
T_{min} = 0.77, *T_{max}* = 0.82

20231 measured reflections
 5466 independent reflections
 4889 reflections with *I* > 2σ(*I*)
R_{int} = 0.076
 θ_{max} = 27.9°, θ_{min} = 1.6°
h = -13→13
k = -24→24
l = -32→32

Refinement

Refinement on *F*²
 Least-squares matrix: full
R [*F*² > 2σ(*F*²)] = 0.059
wR(*F*²) = 0.122
S = 1.27
 5466 reflections
 448 parameters
 26 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
w = 1/[σ²(*F_o*²) + (0.·*P*)² + 43.9582*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.05 e Å⁻³
 Δρ_{min} = -1.43 e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.5000	0.5000	0.5000	0.0618 (4)	
Co2	1.0000	0.56680 (4)	0.7500	0.01690 (16)	
Co3	0.99629 (6)	0.49587 (3)	0.86241 (2)	0.02559 (15)	
O1W	0.4093 (4)	0.5383 (2)	0.56859 (17)	0.0539 (11)	
H1WA	0.441 (5)	0.5763 (16)	0.583 (2)	0.065*	
H1WB	0.340 (2)	0.552 (3)	0.5533 (7)	0.065*	
O2W	0.8698 (3)	0.43158 (18)	0.90284 (14)	0.0359 (8)	
H2WA	0.795 (2)	0.434 (2)	0.889 (2)	0.043*	
H2WB	0.878 (4)	0.3887 (11)	0.914 (2)	0.043*	
O3W	0.1704 (4)	0.31752 (19)	0.36005 (15)	0.0444 (9)	
H3WA	0.163 (4)	0.3570 (16)	0.343 (2)	0.053*	
H3WB	0.245 (2)	0.304 (3)	0.355 (2)	0.053*	
O4W	1.0000	0.3144 (4)	0.7500	0.119 (4)	
H4W	0.946 (6)	0.3420 (12)	0.734 (4)	0.143*	
N11	0.9013 (3)	0.64413 (18)	0.79407 (13)	0.0195 (7)	
N21	0.8065 (4)	0.74782 (19)	0.81202 (15)	0.0288 (8)	
H21	0.782 (5)	0.7913 (10)	0.809 (2)	0.035*	
N31	0.8137 (4)	0.6751 (2)	0.95065 (15)	0.0331 (9)	
N41	0.9017 (3)	0.59333 (19)	0.88509 (13)	0.0239 (7)	
N51	0.7374 (5)	0.7874 (2)	0.92845 (17)	0.0393 (10)	
H51A	0.717 (5)	0.801 (2)	0.9594 (9)	0.047*	
H51B	0.724 (5)	0.8216 (18)	0.9067 (14)	0.047*	
N61	0.8874 (6)	0.5628 (3)	0.97387 (18)	0.0532 (13)	
H61A	0.861 (6)	0.569 (3)	1.0050 (11)	0.064*	
H61B	0.903 (6)	0.5193 (11)	0.968 (2)	0.064*	
C11	0.8600 (4)	0.7070 (2)	0.77525 (17)	0.0247 (9)	
H11	0.8678	0.7212	0.7396	0.030*	
C21	0.8165 (4)	0.7097 (2)	0.85977 (17)	0.0257 (9)	
C31	0.7877 (4)	0.7251 (3)	0.91368 (18)	0.0300 (10)	
C41	0.8670 (4)	0.6126 (3)	0.93572 (18)	0.0308 (10)	
C51	0.8738 (4)	0.6458 (2)	0.84816 (15)	0.0192 (8)	
N12	0.5194 (5)	0.6087 (2)	0.4740 (2)	0.0521 (14)	
N22	0.5759 (5)	0.7002 (2)	0.42269 (19)	0.0435 (11)	
H22	0.599 (5)	0.732 (2)	0.4003 (19)	0.052*	
N32	0.5949 (4)	0.7931 (2)	0.55542 (17)	0.0397 (10)	
N42	0.5265 (5)	0.6701 (2)	0.5605 (2)	0.0487 (12)	
N52	0.6494 (5)	0.8469 (2)	0.47551 (18)	0.0425 (11)	
H52A	0.671 (5)	0.8876 (14)	0.4878 (18)	0.051*	
H52B	0.657 (6)	0.848 (3)	0.4416 (5)	0.051*	
N62	0.5595 (6)	0.7381 (3)	0.6365 (2)	0.0653 (16)	

H62A	0.521 (6)	0.708 (2)	0.656 (2)	0.078*	
H62B	0.547 (7)	0.7789 (14)	0.650 (2)	0.078*	
C12	0.5426 (6)	0.6313 (3)	0.4254 (3)	0.0510 (16)	
H12	0.5364	0.6017	0.3952	0.061*	
C22	0.5737 (5)	0.7256 (2)	0.4757 (2)	0.0371 (12)	
C32	0.6071 (5)	0.7902 (3)	0.5015 (2)	0.0369 (11)	
C42	0.5587 (6)	0.7339 (3)	0.5812 (2)	0.0462 (13)	
C52	0.5393 (5)	0.6683 (3)	0.5057 (2)	0.0428 (13)	
C13	0.7456 (5)	0.5094 (2)	0.58061 (18)	0.0352 (11)	
C23	0.6864 (4)	0.5216 (2)	0.63414 (17)	0.0297 (10)	
H23A	0.6117	0.4914	0.6353	0.036*	
H23B	0.6577	0.5709	0.6351	0.036*	
C33	0.7696 (4)	0.5074 (2)	0.68605 (17)	0.0261 (9)	
C43	0.6950 (4)	0.5242 (2)	0.73587 (18)	0.0278 (9)	
H43A	0.6105	0.5039	0.7309	0.033*	
H43B	0.6860	0.5757	0.7390	0.033*	
C53	0.7567 (4)	0.4952 (2)	0.78852 (18)	0.0304 (10)	
C63	0.8005 (4)	0.4270 (2)	0.68523 (19)	0.0321 (10)	
O13	0.6761 (4)	0.51159 (19)	0.53803 (14)	0.0444 (9)	
O23	0.8635 (3)	0.4991 (2)	0.57762 (13)	0.0404 (8)	
O33	0.8779 (3)	0.49242 (15)	0.79150 (11)	0.0253 (6)	
O43	0.6882 (3)	0.4760 (2)	0.82554 (14)	0.0440 (9)	
O53	0.9030 (3)	0.40625 (16)	0.66689 (13)	0.0318 (7)	
O63	0.7175 (4)	0.38575 (19)	0.70148 (18)	0.0514 (10)	
O73	0.8818 (3)	0.54856 (14)	0.68448 (11)	0.0215 (6)	
O5W	0.5574 (7)	0.6585 (3)	0.3006 (3)	0.117 (3)	
O6W'	0.475 (2)	0.6761 (7)	0.7328 (5)	0.099 (7)	0.392 (13)
O6W''	0.4363 (18)	0.6138 (9)	0.6758 (8)	0.074 (8)	0.273 (14)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0851 (9)	0.0234 (5)	0.0711 (8)	-0.0084 (5)	-0.0602 (7)	0.0102 (5)
Co2	0.0183 (4)	0.0169 (4)	0.0153 (3)	0.000	-0.0017 (3)	0.000
Co3	0.0336 (3)	0.0215 (3)	0.0213 (3)	0.0006 (2)	-0.0026 (2)	0.0052 (2)
O1W	0.056 (2)	0.044 (2)	0.058 (3)	-0.0180 (19)	-0.034 (2)	0.020 (2)
O2W	0.0419 (19)	0.0290 (17)	0.0370 (19)	-0.0009 (15)	0.0049 (15)	0.0110 (15)
O3W	0.056 (2)	0.0322 (19)	0.044 (2)	0.0078 (17)	-0.0126 (18)	0.0105 (16)
O4W	0.188 (10)	0.036 (4)	0.123 (7)	0.000	-0.102 (7)	0.000
N11	0.0233 (17)	0.0205 (16)	0.0147 (15)	0.0030 (13)	0.0015 (13)	0.0046 (13)
N21	0.040 (2)	0.0196 (17)	0.0269 (19)	0.0061 (16)	0.0037 (16)	-0.0010 (15)
N31	0.044 (2)	0.036 (2)	0.0201 (18)	-0.0056 (18)	0.0113 (16)	-0.0015 (16)
N41	0.0291 (19)	0.0260 (18)	0.0169 (16)	-0.0031 (15)	0.0050 (14)	0.0042 (14)
N51	0.056 (3)	0.033 (2)	0.030 (2)	0.001 (2)	0.016 (2)	-0.0013 (18)
N61	0.095 (4)	0.036 (2)	0.030 (2)	0.014 (3)	0.025 (2)	0.014 (2)
C11	0.031 (2)	0.022 (2)	0.022 (2)	-0.0031 (17)	0.0035 (17)	0.0010 (16)
C21	0.028 (2)	0.026 (2)	0.024 (2)	-0.0042 (17)	0.0034 (16)	0.0043 (17)
C31	0.031 (2)	0.033 (2)	0.027 (2)	-0.0044 (19)	0.0085 (18)	-0.0025 (19)
C41	0.034 (2)	0.035 (2)	0.023 (2)	-0.005 (2)	0.0054 (18)	0.0028 (18)

C51	0.0181 (18)	0.0232 (19)	0.0166 (18)	-0.0039 (15)	0.0046 (14)	-0.0004 (15)
N12	0.068 (3)	0.025 (2)	0.060 (3)	-0.001 (2)	-0.043 (3)	0.006 (2)
N22	0.059 (3)	0.026 (2)	0.043 (3)	0.009 (2)	-0.023 (2)	0.0014 (18)
N32	0.054 (3)	0.028 (2)	0.036 (2)	0.0063 (19)	-0.013 (2)	-0.0022 (17)
N42	0.058 (3)	0.033 (2)	0.054 (3)	-0.010 (2)	-0.021 (2)	0.011 (2)
N52	0.064 (3)	0.022 (2)	0.040 (2)	0.001 (2)	-0.014 (2)	-0.0008 (18)
N62	0.090 (5)	0.061 (4)	0.045 (3)	-0.009 (3)	-0.004 (3)	0.009 (3)
C12	0.059 (4)	0.026 (2)	0.065 (4)	0.008 (2)	-0.041 (3)	-0.008 (3)
C22	0.049 (3)	0.024 (2)	0.037 (3)	0.008 (2)	-0.019 (2)	0.001 (2)
C32	0.043 (3)	0.026 (2)	0.041 (3)	0.004 (2)	-0.011 (2)	-0.002 (2)
C42	0.050 (3)	0.044 (3)	0.043 (3)	0.003 (3)	-0.012 (2)	0.004 (2)
C52	0.049 (3)	0.027 (2)	0.050 (3)	0.004 (2)	-0.028 (3)	0.005 (2)
C13	0.053 (3)	0.022 (2)	0.028 (2)	-0.001 (2)	-0.019 (2)	-0.0030 (18)
C23	0.031 (2)	0.030 (2)	0.026 (2)	-0.0001 (18)	-0.0120 (18)	-0.0021 (18)
C33	0.024 (2)	0.026 (2)	0.027 (2)	-0.0045 (18)	-0.0075 (16)	0.0020 (17)
C43	0.020 (2)	0.030 (2)	0.033 (2)	-0.0017 (17)	-0.0047 (17)	0.0029 (18)
C53	0.035 (2)	0.021 (2)	0.035 (2)	-0.0101 (19)	-0.0035 (19)	0.0029 (18)
C63	0.032 (2)	0.026 (2)	0.037 (3)	-0.0039 (19)	-0.0123 (19)	-0.0032 (19)
O13	0.056 (2)	0.040 (2)	0.0338 (18)	0.0032 (17)	-0.0271 (17)	-0.0051 (16)
O23	0.047 (2)	0.048 (2)	0.0255 (17)	0.0049 (18)	-0.0103 (14)	-0.0087 (16)
O33	0.0283 (15)	0.0224 (15)	0.0247 (15)	-0.0038 (12)	-0.0055 (12)	0.0052 (12)
O43	0.0328 (19)	0.058 (2)	0.042 (2)	-0.0093 (17)	0.0059 (15)	0.0205 (18)
O53	0.0367 (18)	0.0199 (15)	0.0382 (18)	-0.0034 (13)	-0.0029 (14)	0.0013 (13)
O63	0.050 (2)	0.0250 (18)	0.080 (3)	-0.0142 (17)	0.004 (2)	0.0009 (18)
O73	0.0242 (14)	0.0191 (14)	0.0204 (14)	-0.0050 (11)	-0.0071 (11)	-0.0013 (11)
O5W	0.132 (6)	0.083 (4)	0.144 (6)	0.038 (4)	0.082 (5)	0.041 (4)
O6W'	0.16 (2)	0.076 (10)	0.061 (11)	0.019 (11)	0.020 (12)	0.020 (7)
O6W''	0.088 (15)	0.046 (10)	0.087 (15)	0.012 (9)	-0.001 (11)	-0.005 (9)

Geometric parameters (Å, °)

Co1—O13	2.055 (3)	C21—C51	1.374 (6)
Co1—O13 ⁱ	2.055 (3)	C21—C31	1.414 (6)
Co1—O1W ⁱ	2.115 (5)	N12—C12	1.310 (8)
Co1—O1W	2.115 (5)	N12—C52	1.374 (7)
Co1—N12	2.143 (4)	N22—C12	1.336 (7)
Co1—N12 ⁱ	2.143 (4)	N22—C22	1.399 (7)
Co2—O73	2.030 (3)	N22—H22	0.850 (10)
Co2—O73 ⁱⁱ	2.030 (3)	N32—C42	1.341 (7)
Co2—N11 ⁱⁱⁱ	2.114 (3)	N32—C32	1.349 (7)
Co2—N11	2.114 (3)	N42—C42	1.335 (7)
Co2—O33 ⁱⁱ	2.184 (3)	N42—C52	1.370 (7)
Co2—O33	2.184 (3)	N52—C32	1.328 (7)
Co3—O73 ⁱⁱ	2.028 (3)	N52—H52A	0.846 (10)
Co3—O23 ⁱⁱ	2.049 (3)	N52—H52B	0.848 (10)
Co3—O2W	2.086 (3)	N62—C42	1.373 (7)
Co3—O33	2.109 (3)	N62—H62A	0.851 (10)
Co3—O53 ⁱⁱ	2.128 (3)	N62—H62B	0.849 (10)
Co3—N41	2.162 (4)	C12—H12	0.9300
O1W—H1WA	0.852 (10)	C22—C52	1.362 (7)

O1W—H1WB	0.848 (10)	C22—C32	1.402 (6)
O2W—H2WA	0.848 (10)	C13—O13	1.257 (5)
O2W—H2WB	0.849 (10)	C13—O23	1.264 (6)
O3W—H3WA	0.851 (10)	C13—C23	1.510 (7)
O3W—H3WB	0.847 (10)	C23—C33	1.546 (5)
O4W—H4W	0.850 (10)	C23—H23A	0.9700
N11—C11	1.328 (5)	C23—H23B	0.9700
N11—C51	1.386 (5)	C33—O73	1.413 (5)
N21—C11	1.334 (5)	C33—C43	1.528 (6)
N21—C21	1.382 (5)	C33—C63	1.536 (6)
N21—H21	0.853 (10)	C43—C53	1.530 (6)
N31—C31	1.327 (6)	C43—H43A	0.9700
N31—C41	1.354 (6)	C43—H43B	0.9700
N41—C51	1.363 (5)	C53—O43	1.248 (5)
N41—C41	1.372 (5)	C53—O33	1.278 (5)
N51—C31	1.338 (6)	C63—O63	1.247 (6)
N51—H51A	0.845 (10)	C63—O53	1.254 (6)
N51—H51B	0.844 (10)	O23—Co ³ⁱⁱ	2.049 (3)
N61—C41	1.337 (6)	O53—Co ³ⁱⁱ	2.128 (3)
N61—H61A	0.839 (10)	O73—Co ³ⁱⁱ	2.028 (3)
N61—H61B	0.842 (10)	O6W'—O6W ⁱⁱⁱ	0.98 (3)
C11—H11	0.9300		
O13—Co1—O13 ⁱ	180.0	N31—C31—N51	119.6 (4)
O13—Co1—O1W ⁱ	88.36 (14)	N31—C31—C21	117.6 (4)
O13 ⁱ —Co1—O1W ⁱ	91.64 (14)	N51—C31—C21	122.7 (4)
O13—Co1—O1W	91.64 (14)	N61—C41—N31	117.5 (4)
O13 ⁱ —Co1—O1W	88.36 (14)	N61—C41—N41	115.1 (4)
O1W ⁱ —Co1—O1W	180.000 (1)	N31—C41—N41	127.5 (4)
O13—Co1—N12	86.64 (15)	N41—C51—C21	124.5 (4)
O13 ⁱ —Co1—N12	93.36 (15)	N41—C51—N11	125.9 (4)
O1W ⁱ —Co1—N12	91.42 (19)	C21—C51—N11	109.6 (3)
O1W—Co1—N12	88.58 (18)	C12—N12—C52	103.7 (4)
O13—Co1—N12 ⁱ	93.36 (15)	C12—N12—Co1	127.3 (4)
O13 ⁱ —Co1—N12 ⁱ	86.64 (15)	C52—N12—Co1	127.5 (4)
O1W ⁱ —Co1—N12 ⁱ	88.58 (18)	C12—N22—C22	105.3 (5)
O1W—Co1—N12 ⁱ	91.42 (19)	C12—N22—H22	141 (4)
N12—Co1—N12 ⁱ	180.000 (1)	C22—N22—H22	113 (4)
O73—Co2—O73 ⁱⁱ	160.68 (16)	C42—N32—C32	118.8 (4)
O73—Co2—N11 ⁱⁱ	89.99 (12)	C42—N42—C52	111.6 (5)
O73 ⁱⁱ —Co2—N11 ⁱⁱ	103.26 (12)	C32—N52—H52A	129 (3)
O73—Co2—N11	103.26 (12)	C32—N52—H52B	123 (3)
O73 ⁱⁱ —Co2—N11	89.99 (12)	H52A—N52—H52B	108 (2)
N11 ⁱⁱ —Co2—N11	93.86 (18)	C42—N62—H62A	124 (5)
O73—Co2—O33 ⁱⁱ	82.51 (11)	C42—N62—H62B	118 (5)
O73 ⁱⁱ —Co2—O33 ⁱⁱ	85.23 (11)	H62A—N62—H62B	105 (2)
N11 ⁱⁱ —Co2—O33 ⁱⁱ	82.82 (12)	N12—C12—N22	114.6 (5)
N11—Co2—O33 ⁱⁱ	173.39 (12)	N12—C12—H12	122.7
O73—Co2—O33	85.23 (11)	N22—C12—H12	122.7

O73 ⁱⁱ —Co2—O33	82.51 (11)	C52—C22—N22	105.3 (4)
N11 ⁱⁱ —Co2—O33	173.39 (12)	C52—C22—C32	119.5 (5)
N11—Co2—O33	82.82 (12)	N22—C22—C32	134.9 (5)
O33 ⁱⁱ —Co2—O33	101.03 (16)	N52—C32—N32	119.9 (4)
O73 ⁱⁱ —Co3—O23 ⁱⁱ	86.92 (13)	N52—C32—C22	123.1 (5)
O73 ⁱⁱ —Co3—O2W	172.59 (13)	N32—C32—C22	116.9 (5)
O23 ⁱⁱ —Co3—O2W	97.14 (14)	N42—C42—N32	128.6 (5)
O73 ⁱⁱ —Co3—O33	84.46 (11)	N42—C42—N62	115.2 (5)
O23 ⁱⁱ —Co3—O33	170.09 (13)	N32—C42—N62	116.2 (5)
O2W—Co3—O33	90.92 (13)	C22—C52—N42	124.3 (5)
O73 ⁱⁱ —Co3—O53 ⁱⁱ	81.12 (12)	C22—C52—N12	111.1 (5)
O23 ⁱⁱ —Co3—O53 ⁱⁱ	85.17 (14)	N42—C52—N12	124.6 (5)
O2W—Co3—O53 ⁱⁱ	93.00 (14)	O13—C13—O23	119.5 (5)
O33—Co3—O53 ⁱⁱ	88.67 (12)	O13—C13—C23	119.0 (5)
O73 ⁱⁱ —Co3—N41	93.08 (12)	O23—C13—C23	121.5 (4)
O23 ⁱⁱ —Co3—N41	96.49 (14)	C13—C23—C33	117.7 (4)
O2W—Co3—N41	92.62 (14)	C13—C23—H23A	107.9
O33—Co3—N41	88.86 (12)	C33—C23—H23A	107.9
O53 ⁱⁱ —Co3—N41	173.90 (13)	C13—C23—H23B	107.9
Co1—O1W—H1WA	115 (5)	C33—C23—H23B	107.9
Co1—O1W—H1WB	98.9 (10)	H23A—C23—H23B	107.2
H1WA—O1W—H1WB	104.9 (16)	O73—C33—C43	112.0 (3)
Co3—O2W—H2WA	112 (3)	O73—C33—C63	110.6 (4)
Co3—O2W—H2WB	130 (3)	C43—C33—C63	109.2 (4)
H2WA—O2W—H2WB	105.4 (17)	O73—C33—C23	109.1 (3)
H3WA—O3W—H3WB	105.1 (17)	C43—C33—C23	110.1 (4)
C11—N11—C51	103.9 (3)	C63—C33—C23	105.6 (3)
C11—N11—Co2	125.6 (3)	C33—C43—C53	113.7 (4)
C51—N11—Co2	130.2 (3)	C33—C43—H43A	108.8
C11—N21—C21	105.8 (4)	C53—C43—H43A	108.8
C11—N21—H21	129 (4)	C33—C43—H43B	108.8
C21—N21—H21	124 (3)	C53—C43—H43B	108.8
C31—N31—C41	119.4 (4)	H43A—C43—H43B	107.7
C51—N41—C41	111.6 (4)	O43—C53—O33	124.0 (4)
C51—N41—Co3	121.1 (3)	O43—C53—C43	119.4 (4)
C41—N41—Co3	127.2 (3)	O33—C53—C43	116.6 (4)
C31—N51—H51A	129 (3)	O63—C63—O53	123.8 (4)
C31—N51—H51B	123 (3)	O63—C63—C33	116.5 (4)
H51A—N51—H51B	108 (2)	O53—C63—C33	119.6 (4)
C41—N61—H61A	121 (4)	C13—O13—Co1	149.4 (4)
C41—N61—H61B	126 (4)	C13—O23—Co3 ⁱⁱ	129.9 (3)
H61A—N61—H61B	111 (3)	C53—O33—Co3	126.8 (3)
N11—C11—N21	114.0 (4)	C53—O33—Co2	123.9 (3)
N11—C11—H11	123.0	Co3—O33—Co2	91.96 (11)
N21—C11—H11	123.0	C63—O53—Co3 ⁱⁱ	109.5 (3)
C51—C21—N21	106.5 (4)	C33—O73—Co3 ⁱⁱ	107.9 (2)
C51—C21—C31	119.4 (4)	C33—O73—Co2	123.6 (2)
N21—C21—C31	134.0 (4)	Co3 ⁱⁱ —O73—Co2	99.10 (12)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, y, -z+3/2$; (iii) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA···N42	0.85 (1)	2.06 (4)	2.766 (6)	140 (6)
O2W—H2WA···O43	0.85 (1)	2.04 (3)	2.773 (5)	144 (4)
N61—H61B···O2W	0.84 (1)	2.32 (4)	3.017 (6)	140 (5)
O4W—H4W···O53	0.85 (1)	2.09 (6)	2.835 (5)	147 (10)
O1W—H1WB···N61 ⁱⁱⁱ	0.85 (1)	2.47 (2)	3.286 (7)	163 (4)
O2W—H2WB···N32 ^{iv}	0.85 (1)	1.96 (1)	2.804 (5)	175 (5)
O3W—H3WA···O73 ⁱ	0.85 (1)	1.94 (1)	2.778 (4)	168 (5)
O3W—H3WB···N62 ⁱ	0.85 (1)	2.20 (2)	3.030 (8)	166 (5)
N21—H21···O63 ^v	0.85 (1)	1.78 (2)	2.607 (5)	162 (5)
N51—H51A···N31 ^{vi}	0.85 (1)	2.31 (1)	3.149 (5)	171 (5)
N61—H61A···O23 ^{vii}	0.84 (1)	2.20 (4)	2.842 (5)	133 (5)
N22—H22···O3W ^{viii}	0.85 (1)	2.05 (2)	2.889 (6)	168 (6)
N52—H52B···O3W ^{viii}	0.85 (1)	2.11 (2)	2.934 (6)	163 (5)
N62—H62A···O6W ^r	0.85 (1)	2.07 (4)	2.834 (16)	149 (6)
N62—H62A···O6W ^r	0.85 (1)	2.05 (3)	2.85 (2)	157 (6)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (iii) $-x+1, y, -z+3/2$; (iv) $-x+3/2, y-1/2, -z+3/2$; (v) $-x+3/2, y+1/2, -z+3/2$; (vi) $-x+3/2, -y+3/2, -z+2$; (vii) $x, -y+1, z+1/2$; (viii) $x+1/2, y+1/2, z$.