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Poly[[diaquabis(μ_2-crotonato-κ^3*O*:*O*,*O*′)(crotonato-κ^2*O*,*O*′)-lanthanum(III)] adenine monosolvate monohydrate]

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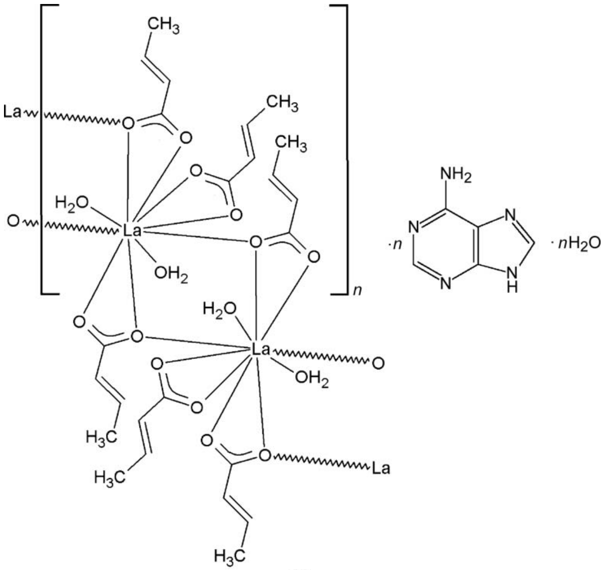
The asymmetric unit of the title compound, $\{[La(C_4H_5O_2)_3(H_2O)_2]\cdot C_5H_5N_5\cdot H_2O\}_n$, consists of an La^{III} cation, three crotonate (but-2-enoate) anions and two coordinated water molecules forming the neutral complex, completed by an external adenine molecule and one hydration water molecule. The LaO_{10} coordination polyhedra, connected through the sharing of a single edge, form isolated chains running along the [100] direction. These one-dimensional structures are characterized by two different centrosymmetric La_2O_2 loops, with La$\cdots$La distances of 4.5394 (6) and 4.5036 (6) Å. The unbound adenine and water solvent molecules form a highly planar hydrogen-bonded array parallel to (110) (r.m.s. deviation from the mean plane < 0.10 Å) which intersects the isolated La–crotonate chains in a slanted fashion to form an extremely connected hydrogen-bonded three-dimensional structure.

Comment

Homonuclear systems with ligands that serve as molecular bridges between metal centres have received considerable attention over the years (Fujita *et al.*, 1994; Lu & Babb, 2001; Thompson, 2002). A point of interest in these systems is the possibility to introduce extra ligands as bridges and thus obtain grid structures and/or clusters, which are appealing not only structurally, but also for their potential application, *e.g.* in ion exchange, catalysis, molecular absorption, optical, electronic and magnetic areas (Ma *et al.*, 2000; Wang *et al.*, 2002; Xu *et al.*, 2002; Benelli & Gatteschi, 2002; Pan *et al.*, 2004). We have for some time focused our attention on the efficiency of crotonic acid (Hcrot or but-2-enoic acid) to couple Ln^{III} ions and as a result we have described the synthesis, structural and magnetic characterization of a number of lanthanide complexes displaying this type of bridge (Rizzi *et al.*, 2003; Baggio *et al.*, 2003, 2005; Atria *et al.*, 2004; Muñoz *et al.*, 2005; Perec *et al.*, 2008).

In parallel, our investigation on carboxylate complexes showed us that the incorporation of some purine derivatives (in our case, 2,6-diaminopurine, dap) might facilitate crystallization, either through their inclusion as neutral cocrystallization agents (Atria *et al.*, 2009) or as counter-ions (Atria, Morel *et al.*, 2011), or even as coordinating ligands (Atria, Corsini *et al.*, 2011; Atria, Garland *et al.*, 2011).

We present herein our first result with adenine (ade), a close relative of dap, which a preliminary literature search [Cambridge Structural Database (CSD), Version 5.32; Allen, 2002] had shown to be equally versatile and which in conjunction with crotonic acid led to the title La complex formulated as $\{[La(crot)_3(H_2O)_2]\cdot ade\cdot H_2O\}_n$, (I). In this complex, the adenine molecule appears unbound, but fulfils an essential role in crystal stabilization.



(I)

Fig. 1 shows the asymmetric unit of (I), which consists of an La1 cation, three crotonate anions and two coordinated water molecules determining the neutral complex, completed by an external adenine molecule and one hydration water molecule. The three crotonate anions (distinguished in their atom labelling by the trailing numbers 1, 2 and 3) act in a chelating manner. Units 1 and 3 have in addition one of their carboxylate O atoms (O11 and O13) shared by neighbouring coordination polyhedra (Fig. 1), thus giving rise to chains which evolve along [100]. In addition to the eight sites thus provided by the carboxylate O atoms to the La environment, there are two extra water O atoms, completing a tenfold coordination. These latter La$-$O$_{aq}$ bonds are very similar in length, as well as being the shortest in the whole set (Table 1); those involving the crotonate anions, instead, present a broader span [2.5562 (16)–2.7815 (16) Å]. The whole coordination assembly resembles a slightly distorted bicapped square antiprism (Fig. 1, inset), with

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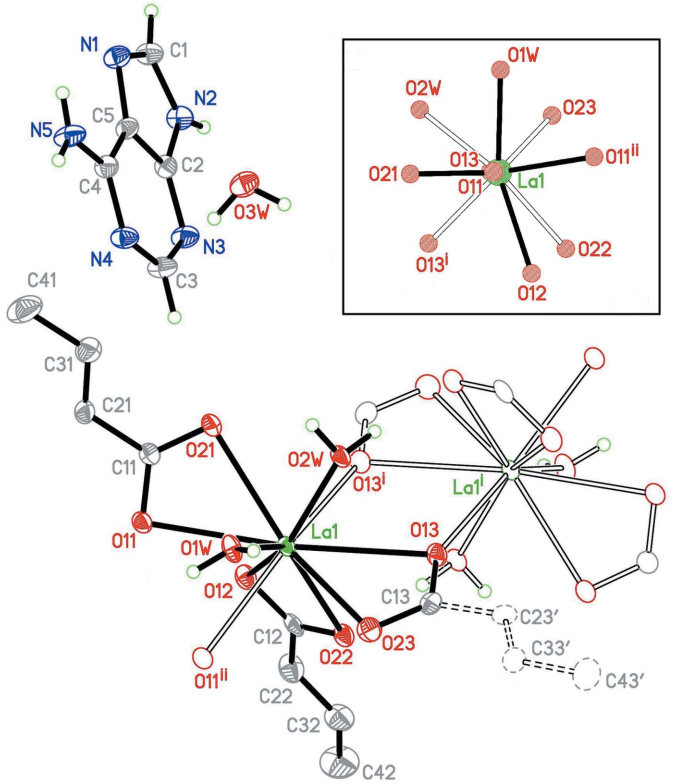


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 40% probability level. Independent (symmetry-related) atoms are drawn with heavy (hollow) bonds and filled (empty) ellipsoids. The double broken lines represent the major component of disordered crotonate 3. Inset: the coordination assembly in the form of a distorted bicapped square antiprism. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.]

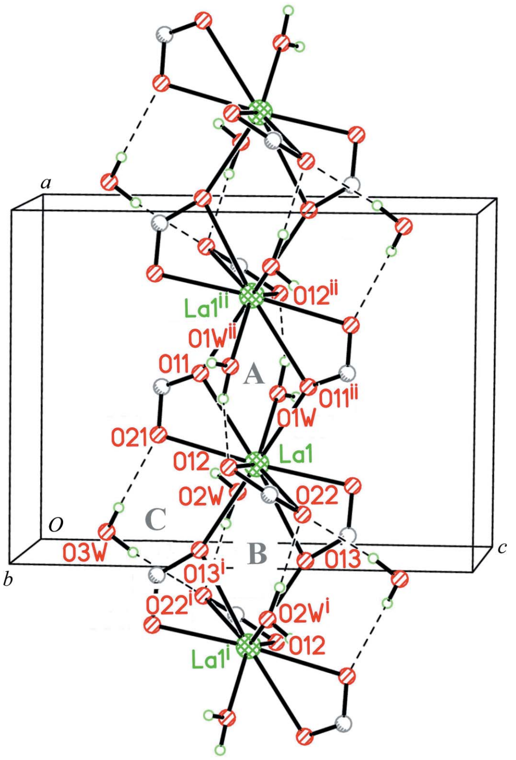


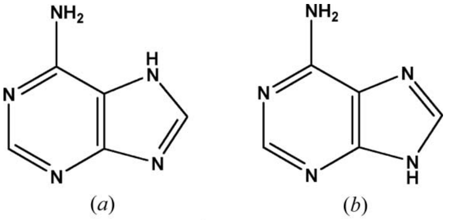
Figure 2
A schematic view of the chains in (I), running along the [100] direction, showing the elementary loops (**A** and **B**) building up the structure. For clarity, the crotonate ligands have been represented by their carboxylate ends only. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.]

atoms O11 and O13 at the apices, defining an almost straight vertical axis [O11—La1—O13 = 173.72 (4)°].

As stated, the $\mu_2\kappa^3$ binding modes displayed by the crot1 and crot3 ligands generate a one-dimensional structure parallel to [100]. Fig. 2 shows a partial view of one of these $[La(crot)_3(H_2O)_2]$ chains. The main motifs are the two different centrosymmetric $(LaO)_2$ loops (**A** and **B** in Fig. 2), leading to La1···La1 intercationic distances of La1···La1^i = 4.5394 (6) Å and La1···La1^{ii} = 4.5036 (6) Å [symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$], and giving the chain a slightly twisted character as measured by the La1^i···La1···La1^{ii} angle of 163.40 (2)° and an interplanar dihedral angle of 38.42 (2)°.

These loops, flanked by two chelating carboxylate groups, act as the only covalent links in the chain. This is a rather unusual fact in Ln–carboxylate chains, where the vast majority of the reported cases present triple or even more complex bridging schemes: out of about 270 polymeric structures with Ln–carboxylate motifs found in the CSD, only six (thus seven including the present structure) show this very simple linking motif. Surprisingly, in three of them the ligand involved is precisely the crotonate anion (Atria *et al.*, 2004; Baggio *et al.*, 2005).

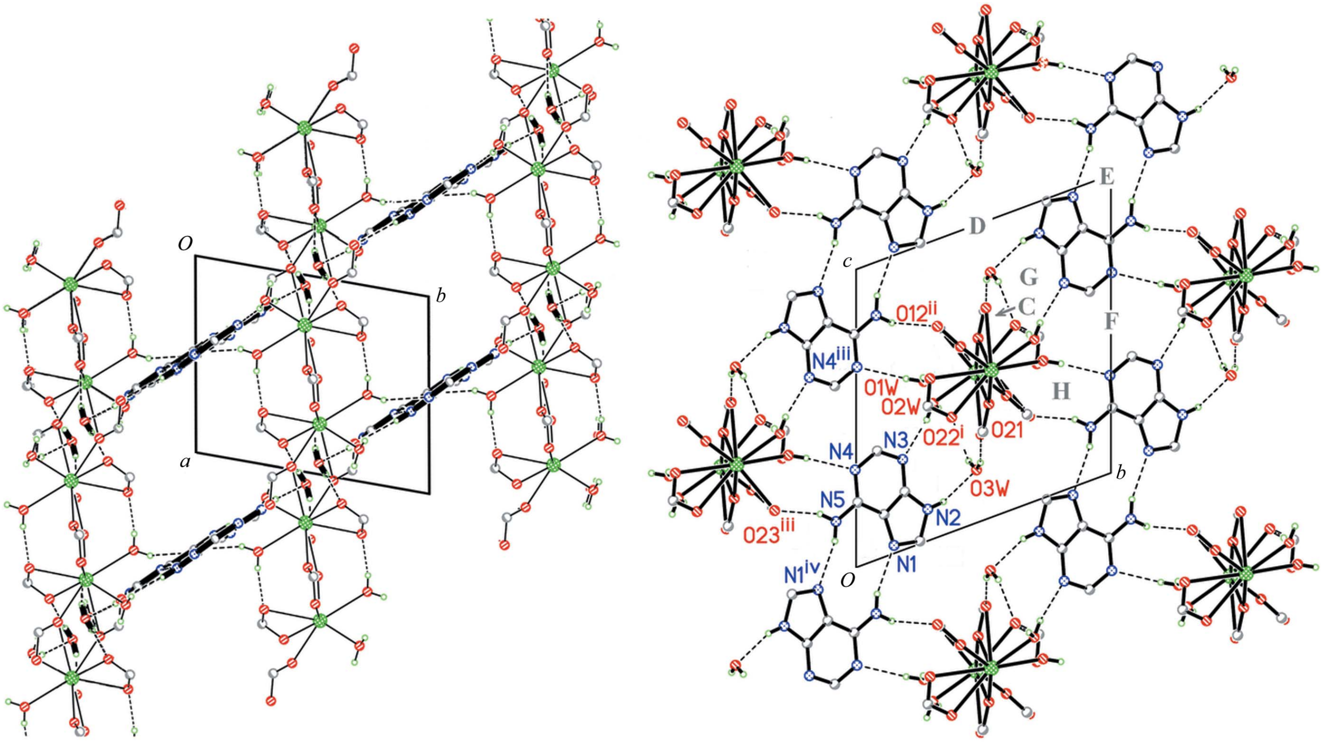
The neutral adenine molecule (hereafter ade^0) does not show any unusual feature from a metrical point of view (see, for instance, Mahapatra *et al.*, 2008), and the distribution of single/double bonds within the ring system corresponds to the most frequent disposition found for the molecule. In fact, ade^0 can present two possible prototropic states, with protonation at either N1 or N2 [see (*a*) and (*b*) in Scheme 2]. A search of the CSD found 24 appearances of an ade^0 unit, one-third of which correspond to form (*a*) and two-thirds to form (*b*), thus confirming the present case as corresponding to the most frequent state.



(*a*) (*b*)

Scheme 2

The molecule does not take part in coordination but, in conjunction with the solvent water, plays an important role in the general cohesion. Both molecules generate a hydrogen-bonded two-dimensional structure which serves as the inter-chain linking agent (see below). The array presents a strikingly planar character (the r.m.s. deviation from the least-squares plane for non-H atoms is 0.10 Å) and lies almost exactly on the crystallographic (220) plane. Planarity is the result of a whole family of inversion centres at r_1 and r_2 being embedded into



(*a*) (*b*)

Figure 3

Two complementary packing views of the structure drawn (*a*) along *c*, with the aqua–La–crotonate chains running vertically, and (in projection) the adenine–water planes connecting them, and (*b*) along *a*, with the aqua–La–crotonate chains (now in projection, coming out of the figure) interconnected through hydrogen bonding by the (slanted) adenine–water planes. The crotonate ligands have been represented only by their carboxylate ends for clarity. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $-x+1, -y, -z$.]

the array [$r_1 = (\frac{1}{2},0,0) + (\frac{1}{2},-\frac{1}{2},0)\,n$; $r_2 = (0,0,\frac{1}{2})\,m$; n and m are integers]. This characteristic guarantees that the adenine molecules are parallel to each other (the result of centrosymmetry) and coplanar (the result of embedding). Fig. 3(*a*) shows in projection the way in which the adenine–water (220) planes intersect the La–crotonate [100] chains, at a slanting angle of 146.0°.

The dense hydrogen-bonding network has the carboxylate O atoms as acceptors and the adenine and water (coordinated as well as hydration) H atoms as donors, generating a number of hydrogen-bonding loops. Full details are given in Table 2, and a general view of the way in which this happens is given in Fig. 3(*b*) [for a survey of graph-set nomenclature of hydrogen-bonding loops, see Bernstein *et al.* (1995)]. Three of the generated loops are centrosymmetric and internal to the chains, thus reinforcing their internal cohesion. They involve the three different water molecules in the asymmetric unit, *viz*. the two coordinated water molecules (in Fig. 2, loop *A* {[O12—La1—O1*W*—H1*WB*···] plus its image at $(-x+1, -y+1, -z+1)$} and loop *B* {[O22—La1—O2*W*—H2*WB*···] plus its image at $(-x, -y+1, -z+1)$}, both with graph-set motif $R_2^2(8)$) and the unbound solvent water molecule (loop *C*, graph-set motif $R_4^4(12)$ {[O22—La1—O21···H3*WA*—O3*W*—H3*WB*···] plus its image at $(-x, -y+1, -z+1)$}).

On the other hand, neighbouring [100] chains in the structure are one unit cell apart in either the *b* or *c* directions, and thus occupy only sparsely the available space in the crystal; the remaining hydrogen bonds serve to link these otherwise non-interacting structures, to define a tight three-dimensional network. These interactions fully involve the adenine N and H atoms. Three of these loops are also centrosymmetric {**D** [$R_8^8(24)$], **E** [$R_2^2(10)$] and **F** [$R_4^4(16)$] in Fig. 3*b*}, while the remaining two loops lie in general positions {**G** [$R_2^2(8)$] and **H** [$R_2^2(10)$] in Fig. 3*b*}.

Experimental

A mixture of La_2O_3 (0. 215 g, 0.66 mmol) and crotonic acid (0.344 g, 4.0 mmol) was dissolved in water (200 ml), followed by the addition of adenine (0.089 g, 0.66 mmol) dissolved in ethanol (40 ml). The resultant mixture was refluxed for 24 h and filtered. The filtrate was left to stand at room temperature. On standing, colourless crystals suitable for single-crystal X-ray diffraction analysis appeared, which were used without further processing. All the reagents and solvents were commercially available and were used without additional purification.

Crystal data

$[La(C_4H_5O_2)_3(H_2O)_2]\cdot C_5H_5N_5\cdot H_2O$
$M_r = 583.34$
Triclinic, $P\bar{1}$
$a = 8.9484$ (11) Å
$b = 11.4743$ (14) Å
$c = 12.3985$ (15) Å
$\alpha = 68.978$ (2)°
$\beta = 84.418$ (2)°
$\gamma = 78.501$ (2)°
$V = 1164.0$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.89$ mm^{-1}
$T = 150$ K
0.46 × 0.25 × 0.18 mm

Table 1
Selected bond lengths (Å).

La1—O1*W*	2.5229 (16)	La1—O12	2.6156 (16)
La1—O2*W*	2.5239 (16)	La1—O21	2.6246 (16)
La1—O13^{i}	2.5562 (16)	La1—O22	2.6419 (15)
La1—O23	2.5789 (17)	La1—O11	2.7002 (16)
La1—O11^{ii}	2.5802 (15)	La1—O13	2.7815 (16)

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

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H2$\cdots$O3*W*	0.852 (10)	1.962 (16)	2.774 (3)	159 (3)
N5—H5*A*$\cdots$O23^{iii}	0.851 (10)	2.149 (14)	2.970 (3)	162 (3)
N5—H5*B*$\cdots$N1^{iv}	0.847 (10)	2.119 (15)	2.927 (3)	159 (3)
O1*W*—H1*WA*$\cdots$N4^{iii}	0.843 (10)	2.033 (16)	2.831 (3)	158 (3)
O1*W*—H1*WB*$\cdots$O12^{ii}	0.845 (10)	1.833 (14)	2.651 (2)	162 (3)
O2*W*—H2*WA*$\cdots$N3	0.844 (10)	1.947 (13)	2.776 (2)	167 (3)
O2*W*—H2*WB*$\cdots$O22^{i}	0.847 (10)	1.887 (10)	2.733 (2)	177 (3)
O3*W*—H3*WA*$\cdots$O21	0.848 (10)	2.254 (15)	3.082 (3)	166 (4)
O3*W*—H3*WB*$\cdots$O22^{i}	0.845 (10)	2.073 (11)	2.914 (3)	173 (3)

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

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS* in *SAINT-NT*; Bruker, 2002)
$T_{\min} = 0.79$, $T_{\max} = 0.89$
6882 measured reflections
4569 independent reflections
4445 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.010$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.057$
$S = 1.05$
4569 reflections
339 parameters
27 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.93$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

One of the crotonate units (trailing number 3) appeared with its tail disordered in two sets of dissimilar populations, which refined to 0.615 (4) and 0.385 (4). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving the disordered C atoms, while the anisotropic displacement factors of the two positions of each disordered atom were constrained to be equal [instructions SADI 0.01 and EADP in *SHELXTL* (Sheldrick, 2008)]. As a result of the disorder, the angles at atom C13, which is bonded to both disordered and nondisordered atoms, ended up having slightly unrealistic values.

H atoms in the ordered part of the structure were clearly seen in a difference Fourier map, but were treated differently in the refinement: H atoms on C atoms were repositioned at their expected locations, and allowed to ride both in coordinates and in isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C—H = 0.95 Å for methine H atoms and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and C—H = 0.98 Å for methyl H atoms]. H atoms attached to N and O atoms were refined with restrained N—H and O—H distances of 0.85 (1) Å and free U_{iso}(H) values.

The *checkCIF* procedure gave a type B alert on the Hirshfeld test involving the La1—O23 pair. Even if not always genuine, this type of alert may be caused by a wrong assignment of some of the involved atomic species. The careful synthetic conditions, as well as a variety of refinement trials with different atomic assignments, proved the alert was, in this case, an artifact.

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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3062). Services for accessing these data are described at the back of the journal.

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