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Two isomorphous crotonatolanthanide complexes: tetra-μ-but-2-enoato-bis-[diaqua(but-2-enoato)Ln]–2,6-diaminopurine (1/2) (Ln = Dy and Ho). Corrigendum

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One of the figures in the paper by Atria, Astete, Garland & Baggio [*Acta Cryst.* (2009), C**65**, m411–m414] is corrected.

In the paper by Atria *et al.* (2009), the 2,6-diaminopurine molecule shown in Fig. 1 is incorrect, with atoms N1, N3 and N7 appearing as protonated. The correct figure is given here. It is worth mentioning that the error only relates to this representation of the molecule; the refined model and the corresponding discussion and packing diagrams as presented in the original paper are correct.

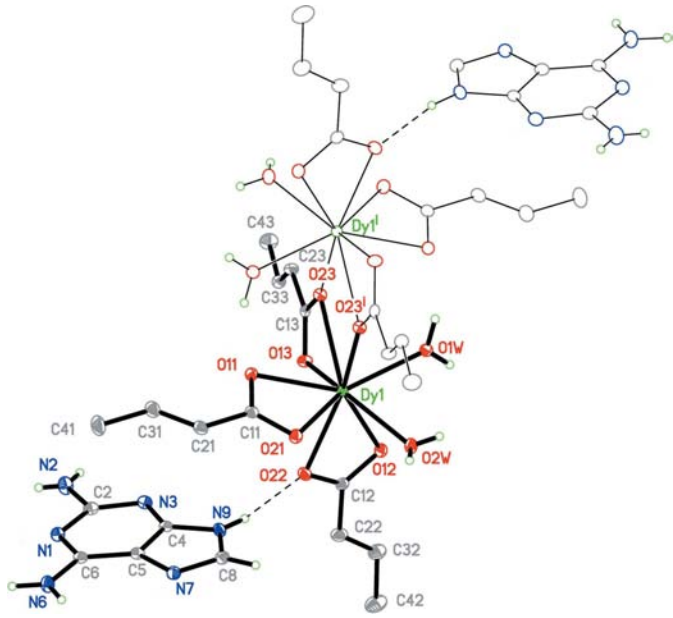

Figure 1
A displacement ellipsoid plot of (I), drawn at the 40% probability level, with independent (symmetry-related) atoms indicated by bold (fine) bonds and filled (empty) ellipsoids. [Symmetry code: (i) $-x$, $-y$, $-z$.]

References

Atria, A. M., Astete, A., Garland, M. T. & Baggio, R. (2009). *Acta Cryst.* C**65**, m411–m414.

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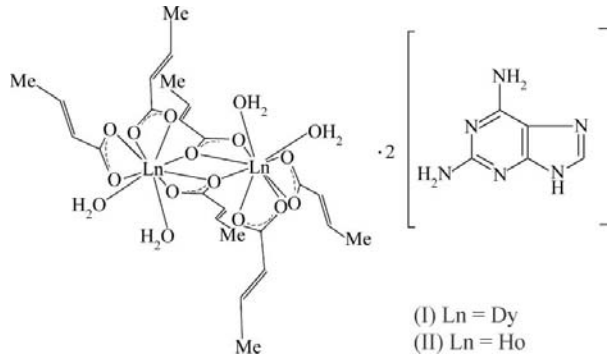
The title isomorphous compounds, tetra-μ-but-2-enoato-bis-[diaqua(but-2-enoato)dysprosium(III)]–2,6-diaminopurine (1/2), $[Dy_2(C_4H_5O_2)_6(H_2O)_4]\cdot 2C_5H_6N_6$, and tetra-$\mu$-but-2-enoato-bis[diaqua(but-2-enoato)holmium(III)]–2,6-diaminopurine (1/2), $[Ho_2(C_4H_5O_2)_6(H_2O)_4]\cdot 2C_5H_6N_6$, consist of $[Ln(crot)_3(H_2O)_2]_2$ dimers (crot is crotonate or but-2-enoate; Ln is the lanthanide cation), built up around inversion centres and completed by 2,6-diaminopurine molecules. The lanthanide cation is coordinated by three chelating crotonate units and two water molecules. One of the chelating carboxylate groups acts also in a bridging mode sharing one O atom with both cations and the final result is a pair of DyO_9 tricapped prismatic polyhedra linked to each other through a central $(Dy-O)_2$ loop. A feature of the structures is the existence of a complex intermolecular interaction scheme involving two sets of tightly interlinked non-intersecting one-dimensional structures, one of them formed by the $[Dy(crot)_3(H_2O)_2]_2$ dimers (running along [100] and linked by O—H···O hydrogen bonds) and the second formed by 2,6-diaminopurine molecules (evolving along [010] linked by N—H···N hydrogen bonds).

Comment

We report here structural work on two isomorphous Ln complexes, formulated as $[Ln(crot)_3(H_2O)_2]_2\cdot 2(dap)$ [crot is crotonate or but-2-enoate, and dap is 2,6-diaminopurine; Ln = Dy for (I) and Ho for (II)]. These are the first cases in which a free unsubstituted 2,6-diaminopurine molecule is reported to take part in a crystal structure, although some closely related substituted analogues have already been the subject of structural work (Singh & Hodgson, 1975; Simundza *et al.*, 1970; Sakore *et al.*, 1969, *etc.*). For the sake of simplicity we shall only describe the Dy isologue, (I), as representative of the pair of compounds, but numerical data for both compounds are freely available in the archived CIF.



The structure for the Dy complex, shown in Fig. 1, consists of $[Dy(crot)_3(H_2O)_2]_2$ dimers, along with 2,6-diaminopurine molecules. The dimer is build up around an inversion centre. The unique Dy cation is coordinated by three chelating crotonate units and two water molecules. One of the O atoms (O23) from one of the crotonate carboxylate groups acts also in a bridging mode, and the result is a pair of DyO_9 polyhedra [with Dy—O distances in the range 2.3457 (17)–2.5257 (17) Å] presenting a tricapped prismatic coordination geometry linked to form a dimer through a central $(Dy-O)_2$ loop leading to a Dy···Dy distance of 4.0407 (2) Å. This type of carboxylate-linked $[Ln(COO)_3(H_2O)_2]_2$ dimer is well known in the literature: we could trace 36 examples in a Cambridge Structural Database search (CSD; 2009 Version; Allen, 2002), the vast majority (22 cases) with acetate and only one (an isomorphous family) with butenoate (Rizzi *et al.*, 2003, Atria *et*

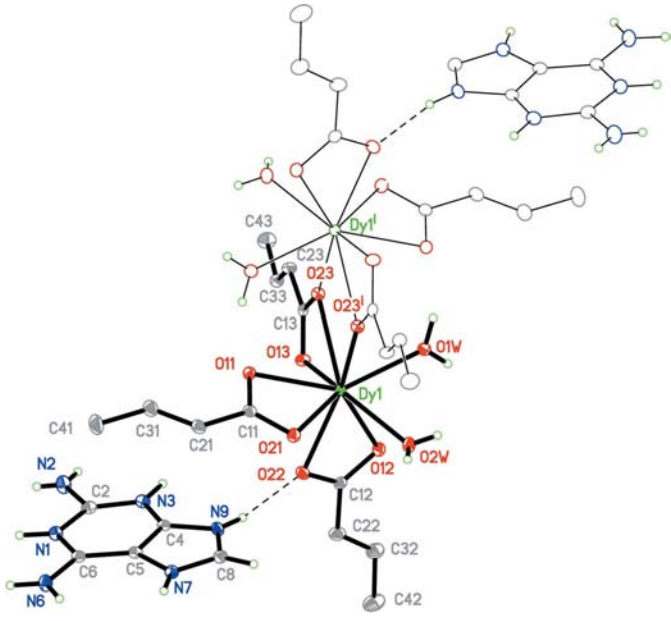


Figure 1
A displacement ellipsoid plot of (I), drawn at the 40% probability level, with independent (symmetry-related) atoms indicated by bold (fine) bonds and filled (empty) ellipsoids. [Symmetry code: (i) $-x, -y, -z$.]

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al., 2006). The dimers are further linked by hydrogen bonding (see below).

The dimensions of the crotonate ligands and 2,6-diaminopurine molecule are normal, with the non-H atoms in the latter lying in a plane (within experimental error). The most significant deviation from planarity is to be found for the amine H atoms, with a conspicuous pyramidal arrangement around N2 (evidencing an N-atom hybridization with a significant sp^3 contribution) and a rather flattened arrangement at N6 (suggesting a predominant sp^2 character). If N-pyramidality is measured by χ_N (the angle between the C—N vector and the NH_2 plane; Allen *et al.*, 1995), for which the ideal values are 0° (for pure sp^2) and 54.7° (for pure sp^3), the corresponding values for both N atoms in the case of (I) are χ_{N2} = 42.3° (mostly sp^3) and χ_{N6} = 15.5° (mostly sp^2). This is consistent with the C2—N2 bond length [1.360 (3) Å] being longer than the C6—N6 bond length [1.346 (3) Å], suggesting a smaller delocalization in the former. The existence of a large number of efficient hydrogen-bonding donors and acceptors in the structure leads to a complex intermolecular interaction scheme involving two sets of tightly interlinked non-intersecting hydrogen-bonded one-dimensional structures, one of

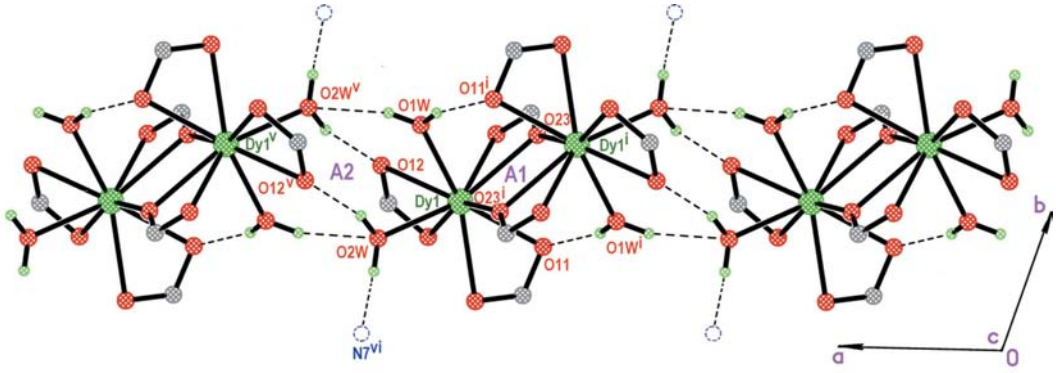

Figure 2
A view of the packing of (I), projected down *c*, showing the chains of dimers and their internal hydrogen-bonding linkage (see *Comment*). For clarity, only the carboxylate end of the butenoate units have been drawn. [Symmetry codes: (i) $-x$, $-y$, $-z$; (v) $-x+1$, $-y$, $-z$.]

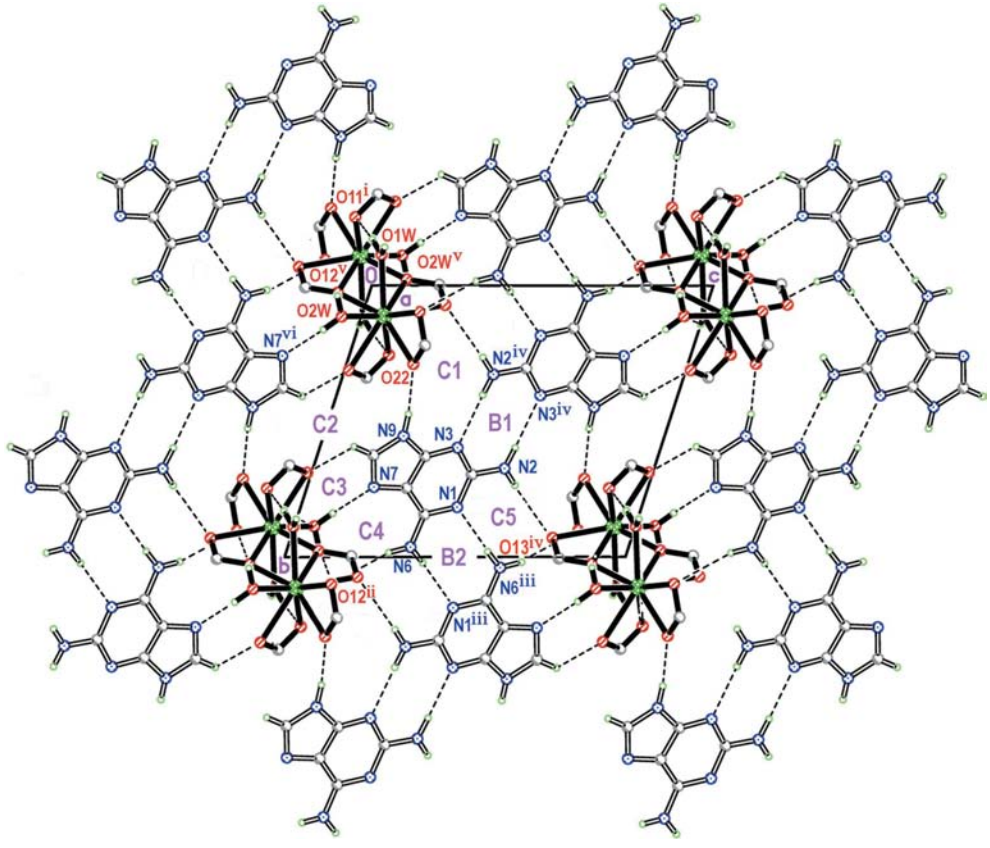

Figure 3
A view of the packing of (I), projected along the *a* axis, showing on the projection plane (running vertically, in hollow bonds) the 'solvate' chains. The chains of dimers are perpendicular to the latter and are shown coming out of the plane of the page (in bold, full bonds). Intra- and inter-chain hydrogen bonds are shown as broken lines. For clarity, only the carboxylate ends of the butenoate units have been drawn. [Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) x, $y+1$, z; (iii) $-x+1$, $-y+2$, $-z+1$; (iv) $-x+1$, $-y+1$, $-z+1$; (v) $-x+1$, $-y$, $-z$; (vi) $-x+1$, $-y+1$, $-z$; (vii) $x-1$, $y-1$, z.]

them running along the crystallographic *a*-axis direction and formed by the $[Dy(crot)_3(H_2O)_2]_2$ dimers, the second evolving along the *b*-axis direction and formed by 2,6-diaminopurine molecules.

Both types of chains contain two sets of inversion centres. In the case of the chain of dimers shown in Fig. 2, the same centre (site *A*1) that relates the two molecules in the dimer through a four-atom coordination loop also links them through an $R_2^2(8)$ hydrogen-bonded ring (Bernstein *et al.*, 1995), almost at right angles to the former loop, *via* O1*W*—H1*WA*···O11^{i} hydrogen bonds (Table 1). The second centre (site *A*2) links neighbouring dimers into chains through two centrosymmetric $R_2^2(8)$ motifs involving O1*W*—H1*WB*···O2*W*^{v} and O2*W*—H2*A*···O12^{v} hydrogen bonds (Table 1), as well as two non-centrosymmetric $R_2^2(6)$ motifs. A much simpler situation arises in the 2,6-diaminopurine chain (Fig. 3), which also utilizes two independent inversion centres and gives rise to two almost identical centrosymmetric $R_2^2(8)$ motifs involving N2—H2*A*···N3^{iv} and N6—H6*A*···N1^{iii} hydrogen bonds, denoted as *B*1 and *B*2 in Fig. 3.

The two perpendicular non-intersecting families of chains (the chain of dimers, running parallel to [100] at $y \simeq z \simeq 0$, and the 2,6-diaminopurine one, parallel to [010] at $x \simeq z \simeq \frac{1}{2}$) interact at their point of maximal approach through a variety of hydrogen bonds in which there are donors and acceptors on both sides (Fig. 3 and Table 1). These hydrogen bonds give rise to four noncentrosymmetric hydrogen-bonded rings with graph-set descriptors $R_3^3(10)$ (site *C*1 in Fig. 3), $R_2^2(7)$ (site *C*3), $R_3^2(9)$ (site *C*4) and $R_3^3(10)$ (site *C*5), and one centrosymmetric ring at site *C*2 with graph-set descriptor $R_4^4(14)$.

There are also inter-dimeric interactions of the π–π type mediated by symmetry-related crotonate double bonds, as in the case between C21=C31 and its $(-x, -y+1, -z)$ image, characterized by an intercentroid distance of 3.588 (1) Å and a slippage angle of 26.6 (1)°. These interactions link along the [001] direction the dimeric chains that run along [100].

Experimental

Complexes (I) and (II) were synthesized by similar methods. A mixture of Ln_2O_3 (Ln = Dy or Ho, 1 mmol) and crotonic acid (3 mmol) was dissolved in water (100 mmol), and then 2,6-diaminopurine (1 mmol) dissolved in methanol (10 ml) was added. The resulting mixture was refluxed for 24 h, filtered while hot and then concentrated to 25 ml. The filtrate was left at room temperature. On standing, colourless crystals suitable for single-crystal X-ray diffraction appeared, which were used without further processing.

Compound (I)

Crystal data

$[Dy_2(C_4H_5O_2)_6(H_2O)_4]\cdot 2C_5H_6N_6$
M_r = 1207.86
Triclinic, $P\overline{1}$
a = 8.6441 (2) Å
b = 11.1173 (3) Å
c = 13.3944 (3) Å
α = 101.234 (2)°
β = 107.521 (3)°
γ = 106.587 (2)°
V = 1119.51 (5) Å^3
Z = 1
Mo *Kα* radiation
μ = 3.39 mm^{-1}
T = 150 K
0.18 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.60, T_{max} = 0.71
9254 measured reflections
4676 independent reflections
4487 reflections with $I > 2\sigma(I)$
R_{int} = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.047
S = 1.06
4676 reflections
292 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Compound (II)

Crystal data

$[Ho_2(C_4H_5O_2)_6(H_2O)_4]\cdot 2C_5H_6N_6$
M_r = 1212.72
Triclinic, $P\overline{1}$
a = 8.644 (2) Å
b = 11.141 (3) Å
c = 13.412 (3) Å
α = 101.360 (3)°
β = 107.537 (4)°
γ = 106.518 (4)°
V = 1122.9 (5) Å^3
Z = 1
Mo *Kα* radiation
μ = 3.58 mm^{-1}
T = 150 K
0.22 × 0.18 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.40, T_{max} = 0.65
8804 measured reflections
4612 independent reflections
4337 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.072
S = 1.35
4612 reflections
292 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.52 e Å^{-3}
$\Delta\rho_{min}$ = −1.73 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H9···O22	0.88	1.91	2.775 (3)	166
N6—H6*B*···O12^{i}	0.88	2.43	3.257 (3)	157
N6—H6*A*···N1^{ii}	0.88	2.42	3.300 (3)	175
N2—H2*A*···N3^{iii}	0.88	2.32	3.190 (3)	171
N2—H2*B*···O13^{iii}	0.88	2.43	3.256 (3)	158
O1*W*—H1*WB*···O2*W*^{iv}	0.84	2.22	2.987 (2)	152
O1*W*—H1*WA*···O11^{v}	0.85	1.91	2.716 (2)	159
O2*W*—H2*WB*···N7^{vi}	0.85	1.84	2.681 (3)	176
O2*W*—H2*WA*···O12^{iv}	0.84	1.87	2.683 (2)	163
C8—H8···O21^{vi}	0.95	2.37	3.128 (3)	136
C23—H23···N7^{vii}	0.95	2.60	3.525 (3)	164
C33—H33···N1^{iii}	0.95	2.57	3.469 (3)	157

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

All H atoms were clearly seen in a difference Fourier map; C—H and (non-amino) N—H groups were, however, subsequently idealized at their expected positions and allowed to ride (C—H = 0.93–0.98 Å and N—H = 0.88 Å). Amino N atoms were in a partially hybridized state, N6 being mostly sp^2 and N2 being mostly sp^3; the corresponding H-atom geometry around these N atoms followed this scheme, with a distorted planar environment around N6 and an important pyramidalization around N2. These H atoms, as well as those corresponding to water molecules, were refined with metric restraints for a few cycles, after which they were allowed to ride. For all H atoms, $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl C).

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3130). Services for accessing these data are described at the back of the journal.

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