

## Two isomorphous lanthanide crotonate complexes: di- $\mu$ -but-2-enoato-bis[di-aquabis(but-2-enoato)dysprosium(III)] adenine monosolvate heptahydrate and the samarium(II) analogue

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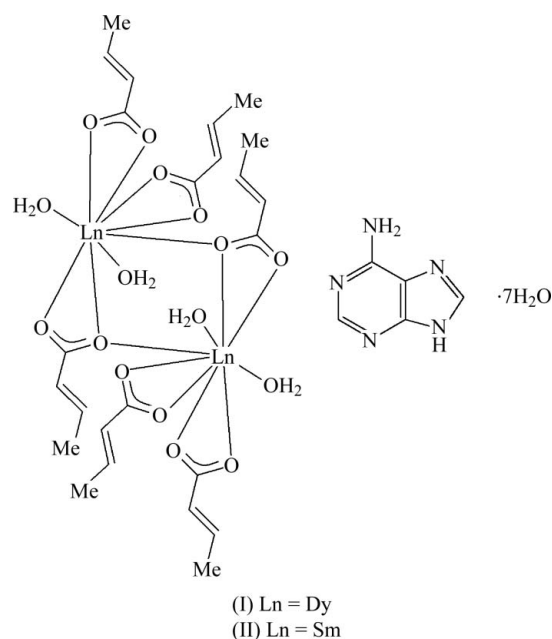
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The asymmetric unit of the title dimeric compounds,  $[\text{Ln}_2(\text{C}_4\text{H}_5\text{O}_2)_6(\text{H}_2\text{O})_4] \cdot \text{C}_5\text{H}_5\text{N}_5 \cdot 7\text{H}_2\text{O}$ , with Ln = Dy, (I), and Sm, (II), consists of an  $\text{Ln}^{\text{III}}$  cation, three crotonate (but-2-enoate) anions and two coordinated water molecules forming the neutral complex, cocrystallized with half of an external adenine molecule and 3.5 water molecules. The metal complex has crystallographic inversion symmetry. The  $\text{LnO}_9$  coordination polyhedra are connected through the sharing of a single edge to form isolated dimeric units, with  $\text{Ln} \cdots \text{Ln}$  separations of 4.1766 (12) Å for (I) and 4.2340 (12) Å for (II). The unbound adenine molecule and one of the solvent water molecules are disordered around an inversion centre into two overlapping, equally populated, units. The structure is sustained by a complex hydrogen-bonding scheme involving all possible O—H and N—H groups as donors, and crotonate and water O and adenine N atoms as acceptors. The system is compared with recently published related compounds.

### Comment

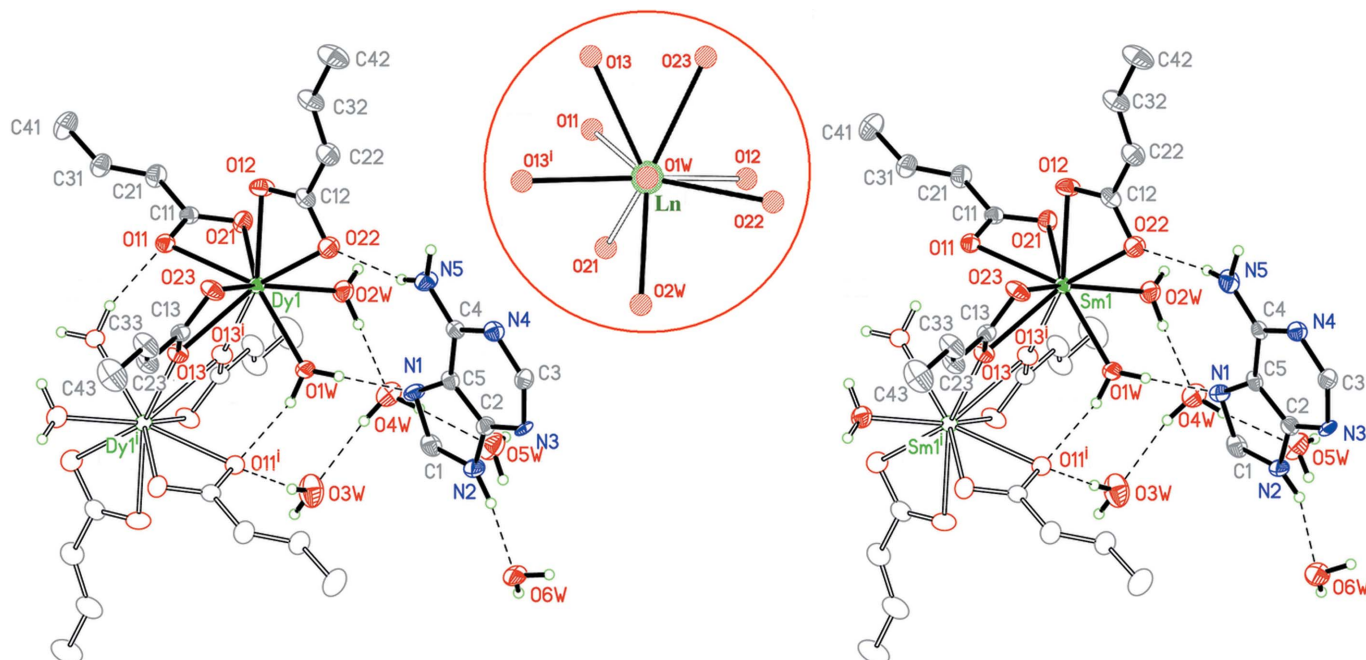
Homonuclear systems with ligands that serve as molecular bridges between the metal centres have received considerable attention through the years (Fujita *et al.*, 1994; Lu & Babb, 2001; Thompson, 2002). A point of interest in these systems is the possibility of introducing extra ligands as bridges and thus obtaining grid structures and/or clusters, which are appealing not only structurally but also for their potential application 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 (but-2-enoic acid, Hcrot) to couple  $\text{Ln}^{\text{III}}$  ions, and as a result we have described the synthesis and structural and magnetic characterization of a number of lanthanide complexes displaying these types of bridges. In parallel, our investigation of carboxylate complexes has showed that the incorporation of some purine derivatives, like 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 & Baggio, 2011). We also tried adenine (ade) and the first outcome with this ligand [an La complex with a one-dimensional structure,  $\{\text{La}(\text{crot})_3(\text{H}_2\text{O})_2(\text{ade}) \cdot \text{H}_2\text{O}\}_n$ , (III)] has been described recently (Atria *et al.*, 2012).



We present herein another example of the crotonate–adenine system, *viz.* the title Ln dimers, formulated as  $\text{Ln}_2(\text{crot})_6(\text{H}_2\text{O})_4 \cdot \text{ade} \cdot 7\text{H}_2\text{O}$ , with Ln = Dy in (I) and Ln = Sm in (II). The two structures are isomorphous and accordingly we shall discuss only one of them in detail, *i.e.* (I), with only marginal reference to the second, *i.e.* (II).

Fig. 1 shows the centrosymmetric dimeric unit for both (I) and (II). The asymmetric unit consists of an  $\text{Ln}^{\text{III}}$  cation, three crotonate anions and two coordinated water molecules determining the neutral complex, completed by an external adenine molecule, disordered around an inversion centre, a solvent water molecule in similar conditions and three further, fully occupied, solvent water molecules. The three crotonate anions (distinguished by the trailing number 1, 2 or 3) act in a chelating way. Unit 3 has, in addition, one of its carboxylate O atoms (O13) shared with a neighbouring coordination polyhedron (Fig. 1), thus giving rise to the central  $\text{Ln}_2\text{O}_2$  loop defining the dimeric unit, with  $\text{Ln} \cdots \text{Ln}$  separations of 4.1766 (12) Å for (I) and 4.2340 (12) Å for (II). The seven sites thus provided to the cation environment by the carboxylate O atoms are expanded by two aqua O atoms to a nine-coordinated polyhedron, with Ln—O bond-length ranges



**Figure 1**

The molecular structures of (I) (left) and (II) (right). Displacement ellipsoids are drawn at the 40% probability level, with independent (symmetry-related) atoms in heavy (hollow) bonds and filled (empty) ellipsoids. Inset: the coordination assembly of the lanthanide cation, with upper and lower coordination planes represented by heavy and hollow bonds, respectively. C-bound H atoms have been omitted for clarity. [Symmetry code: (i)  $-x + 1, -y + 1, -z$ .]

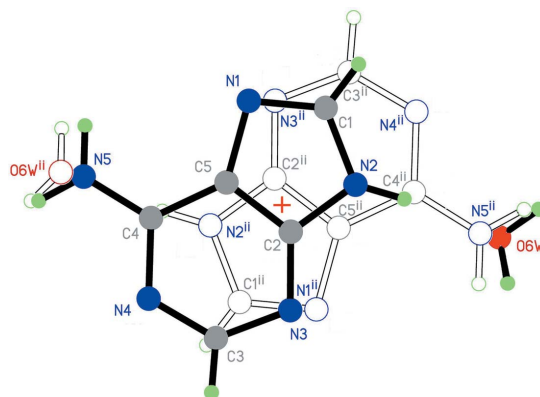
of 2.3504 (19)–2.5524 (19) Å for (I) and 2.4057 (16)–2.5739 (15) Å for (II) (see Tables 1 and 3 for details). The dimeric linkage is reinforced by a strong intra-dimer hydrogen bond involving atoms O1W and O11' [symmetry code: (i)  $-x + 1, -y + 1, -z$ ; Tables 2 and 4, first entry].

This type of dimeric unit occurs rather frequently among Ln crotonates. In particular, we have recently found it in our structural study of the family of lanthanide crotonate diaminopurine analogues, *viz.* di- $\mu$ -but-2-enoato-bis[di-aqua-bis(but-2-enoato)Ln] 2,6-diaminopurine disolvate, with Ln = Ho or Dy [(IV); Atria *et al.*, 2009], or Ln = Nd (Atria, Astete *et al.*, 2011), where the [Ln(crot)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> dinuclear structure is extremely similar to the present one. However, the coordination environments and the resulting hydrogen-bonding schemes are different, and this will be commented on below in the light of the electronic state of their constituents.

The La–adenine analogue, (III), presents a different configuration around the cation, with two carboxylates sharing one of their coordinated O atoms with neighbouring cations, giving rise to chains (instead of dimers) of ten-coordinated (instead of nine-coordinated) polyhedra. The LaO<sub>10</sub> coordination assembly in (III) is a slightly distorted bicapped square antiprism. In contrast, the LnO<sub>9</sub> coordination in (I) and (II) consists of five O atoms in equatorial positions, describing a rather planar structure [mean deviation = 0.112 (2) Å], capped by one O atom above the plane and a triangular array below (Fig. 1, inset). The Dy cation, in turn, lies 0.502 (2) Å below the pentagonal mean plane.

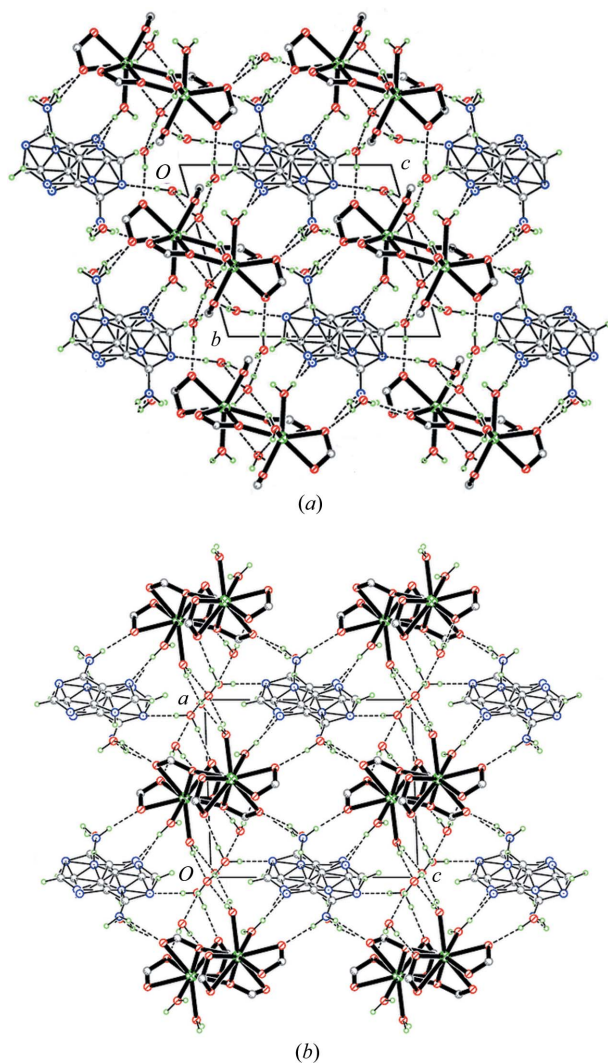
The neutral adenine molecule (hereinafter ade<sup>0</sup>) is basically planar, with a maximum deviation of 0.042 Å for atom N5, and it almost engulfs an inversion centre, 0.0329 (2) Å from the

least-squares plane (shown as a cross in Fig. 2). In addition, the solvent water molecule O6W is also quasi-coplanar [deviation = 0.2620 (12) Å], and so both the adenine molecule and this solvent water molecule are forced to be 0.50:0.50 disordered around the inversion centre. Their symmetry-related images superimpose in such a way that the NH<sub>2</sub> group in one of the images almost coincides with the H<sub>2</sub>O group in the other (Fig. 2). The metrics of the ade<sup>0</sup> group are normal, and it presents the same prototropic state (distribution of single and double bonds) as in the La analogue [Atria *et al.*, 2012; form (b) in Scheme 2 of that work] with protonation at N2. We shall not discuss the point further here, but the interested reader is referred to this latter report for a brief discussion of the subject. The molecule does not take part in



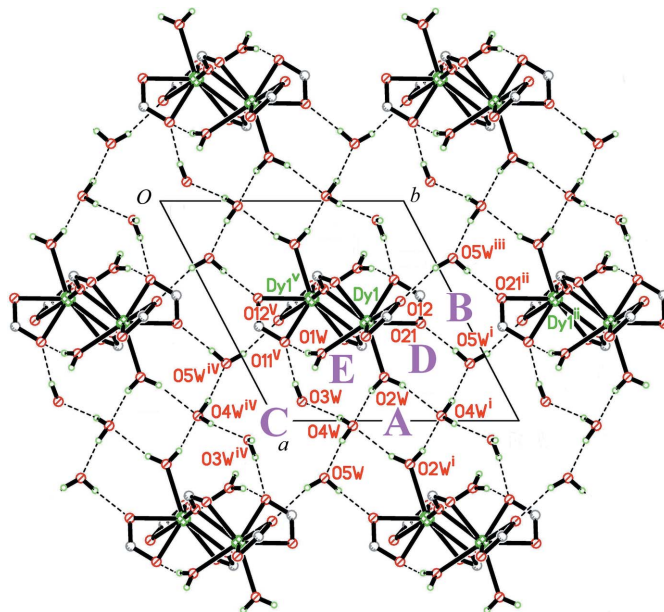
**Figure 2**

A schematic view showing the way in which the disordered adenine and O6W solvent water molecule overlap. [Symmetry code: (ii)  $-x + 2, -y, -z + 1$ .]



**Figure 3**  
Packing views of (I), shown (a) projected down [100] and (b) projected down [010]. C-bound H atoms have been omitted for clarity.

coordination but it plays, in conjunction with the solvent water molecules, a significant role in the general cohesion. Table 2 presents the hydrogen-bonding interactions, in which all available O—H and N—H groups act as donors and all possible O and N atoms act as acceptors; the exceptions to this are based on steric impossibilities, *viz.* shielding (between atoms O1W and O2W, both coordinated to Dy1, and O13, engaged in the Dy—O—Dy bridge) or protonation (on the nitrogen side, only protonated atoms N2 and N5 do not accept hydrogen bonds). Figs. 3(a) and 3(b) present two different views of the web-like structure woven by these interactions, which hold the isolated dimers in place. Simple inspection of these figures shows that both the dimers and most of the solvent water molecules lie in planar arrays parallel to (001) at  $z = 0$ , shown in both views in projection as horizontal strips with heavy lines. In addition, the disordered  $\text{ade}^0$  and O6W molecules serve as connectors between these two-dimensional structures; this linkage is achieved through the hydrogen bonds described by entries 2 to 10 in Table 2. The internal



**Figure 4**  
An [001] packing view of a thin (001) slab of (I), centred at  $z = 0$  and showing the different hydrogen-bonding loops connecting the dimers. Centrosymmetric loops: **A** is  $L_1$  [O4W $\cdots$ H2WB—O2W—H2WA] +  $L_1^i$ , **B** is  $L_2$  [O21—Dy1—O12 $\cdots$ (H5WB—O5W—H5WA) $^{iii}$ ] +  $L_2^{ii}$  and **C** is  $L_3$  [(O12—Dy1—O11) $^v$  $\cdots$ H3WA—O3W $\cdots$ H4WB—O4W—H4WA $\cdots$ O5W—H5WB] +  $L_3^{iv}$ . Noncentrosymmetric loops: **D** is O21—Dy1—O2W—H2WA $\cdots$ (O4W—H4WA $\cdots$ O5W—H5WA) $^i$  and **E** is H2WB—O2W—Dy1—O13—(Dy1—O11) $^v$  $\cdots$ H3WA—O3W $\cdots$ H4WB—O4W. C-bound H atoms have been omitted for clarity. [Symmetry codes: (i):  $-x + 2, -y + 1, -z$ ; (ii):  $-x + 1, -y + 2, -z$ ; (iii):  $x - 1, y + 1, z$ ; (iv):  $-x + 2, -y, -z$ ; (v):  $-x + 1, -y + 1, -z$ .]

cohesion of the planes (made up of dimers and solvent water molecules) is in turn achieved by a large number of hydrogen bonds involving only water H atoms as donors on one side and water and carboxylate O atoms as acceptors on the other (entries 11 to 17 in Tables 2 and 4). Fig. 4 shows a thin (001) layer around  $z = 0$  (thus excluding the disordered part at  $z \sim 0.50$ ), where the most significant hydrogen-bonding loops (**A** to **E**) arising from these interactions are identified. There are three centrosymmetric loops, *viz.* **A**, graph-set  $R_4^2(8)$  (Bernstein *et al.*, 1995), **B**,  $R_4^4(12)$ , and **C**,  $R_4^4(20)$ ; and two noncentrosymmetric loops, *viz.* **D**,  $R_3^3(8)$ , and **E**,  $R_3^3(10)$ .

The present Dy structure, (I), with its very complex interaction scheme involving all available coordinated O atoms, provides an example of the influence which the hydrogen-bonding interactions might have on the O-atom coordination capabilities and even the valence state of the coordinated cations, as second-order receptors of these interactions. In this respect, it is worth comparing the structure of (I) with the above-mentioned Dy diamine purine analogue, (IV), which presents an almost identical dimeric structure but a looser hydrogen-bonding 'web'. For the sake of comparison, some relevant values are, in the order (I)/(IV): (a) overall Dy—O coordination range = 2.3504 (19)—2.5524 (19)/2.3457 (17)—2.5257 (17) Å; (b) bridging Dy $\cdots$ Dy = 4.1766 (12)/4.0412 (13) Å; (c) shortest Dy—O bridge = 2.3784 (18)/2.3464 (17) Å; (d) longest Dy—O bridge = 2.5524 (19)/2.5021 (17) Å. All these data point to a stronger involvement

in coordination in (IV) (with weaker and sparser hydrogen bonds) compared with (I) (showing a stronger and denser hydrogen-bonding network), a fact confirmed by a bond-valence calculation for Dy (using *PLATON*; Spek, 2009), resulting in 2.94 valence units for (IV) versus 2.81 valence units for (I).

## Experimental

Complexes (I) and (II) were synthesized by similar methods. A mixture of the appropriate oxide (Dy<sub>2</sub>O<sub>3</sub> or Sm<sub>2</sub>O<sub>3</sub>, 1 mmol) and crotonic acid (6 mmol) was dissolved in water (100 ml), followed by the addition of the adenine ligand (1 mmol) dissolved in ethanol (40 ml). The resulting mixture was refluxed for 24 h, filtered while hot and then concentrated to 25 ml by evaporation at room temperature. The filtrate was left to stand at room temperature and crystals suitable for single-crystal X-ray diffraction appeared. These were used without further processing.

### Compound (I)

#### Crystal data

[Dy(C <sub>4</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>6</sub> (H <sub>2</sub> O) <sub>4</sub> ].C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> ·7H <sub>2</sub> O	$\beta = 83.958 (5)^\circ$
$M_r = 1168.80$	$\gamma = 61.833 (5)^\circ$
Triclinic, <i>P</i> $\bar{1}$	$V = 1096.1 (5) \text{ \AA}^3$
$a = 10.614 (3) \text{ \AA}$	$Z = 1$
$b = 10.808 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.338 (3) \text{ \AA}$	$\mu = 3.47 \text{ mm}^{-1}$
$\alpha = 73.075 (4)^\circ$	$T = 291 \text{ K}$
	$0.22 \times 0.20 \times 0.12 \text{ mm}$

**Table 1**

Selected bond lengths (Å) for (I).

Dy1—O1W	2.3504 (19)	Dy1—O21	2.4380 (19)
Dy1—O13 <sup>i</sup>	2.3784 (18)	Dy1—O11	2.4456 (19)
Dy1—O12	2.4142 (19)	Dy1—O23	2.4763 (19)
Dy1—O2W	2.428 (2)	Dy1—O13	2.5524 (19)
Dy1—O22	2.429 (2)		

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

**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>
O1W—H1WB...O11 <sup>i</sup>	0.85 (3)	1.99 (3)	2.807 (3)	162 (3)
N2—H2...N5 <sup>ii</sup>	0.85 (3)	1.47 (3)	2.278 (14)	158 (11)
N2—H2...O6W	0.85 (3)	1.86 (3)	2.663 (14)	156 (10)
N5—H5A...O23 <sup>iii</sup>	0.85 (3)	2.28 (3)	2.99 (2)	143 (8)
N5—H5B...O22	0.85 (3)	2.13 (3)	2.95 (2)	161 (7)
O6W—H6WA...O22 <sup>ii</sup>	0.85 (3)	1.96 (3)	2.80 (2)	172 (7)
O6W—H6WB...O23 <sup>iv</sup>	0.85 (3)	1.98 (3)	2.779 (19)	156 (8)
O3W—H3WB...N4 <sup>v</sup>	0.85 (3)	1.90 (3)	2.749 (5)	178 (4)
O1W—H1WA...N1	0.85 (3)	1.89 (3)	2.742 (19)	176 (3)
O1W—H1WA...N3 <sup>ii</sup>	0.85 (3)	2.03 (3)	2.857 (16)	165 (3)
O2W—H2WA...O4W <sup>vi</sup>	0.85 (3)	2.18 (3)	3.001 (3)	163 (3)
O2W—H2WB...O4W	0.85 (3)	1.99 (3)	2.814 (3)	164 (3)
O3W—H3WA...O11 <sup>i</sup>	0.85 (3)	1.96 (3)	2.806 (3)	173 (5)
O4W—H4WA...O5W	0.85 (3)	1.88 (3)	2.724 (3)	170 (4)
O4W—H4WB...O3W	0.85 (3)	2.05 (3)	2.890 (4)	168 (3)
O5W—H5WB...O12 <sup>iv</sup>	0.85 (3)	2.06 (3)	2.879 (3)	164 (4)
O5W—H5WA...O21 <sup>vi</sup>	0.85 (3)	1.98 (3)	2.820 (3)	176 (4)

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

#### Data collection

Bruker SMART CCD area-detector diffractometer	8551 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> in <i>SAINT-NT</i> ; Bruker, 2002)	4253 independent reflections
$T_{\min} = 0.42, T_{\max} = 0.66$	4178 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.046$	$\Delta\rho_{\text{max}} = 0.86 \text{ e \AA}^{-3}$
$S = 1.09$	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
4253 reflections	
365 parameters	
22 restraints	

### Compound (II)

#### Crystal data

[Sm(C <sub>4</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>6</sub> (H <sub>2</sub> O) <sub>4</sub> ].C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> ·7H <sub>2</sub> O	$\beta = 83.926 (4)^\circ$
$M_r = 1144.50$	$\gamma = 61.784 (5)^\circ$
Triclinic, <i>P</i> $\bar{1}$	$V = 1107.7 (5) \text{ \AA}^3$
$a = 10.633 (3) \text{ \AA}$	$Z = 1$
$b = 10.847 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.397 (3) \text{ \AA}$	$\mu = 2.71 \text{ mm}^{-1}$
$\alpha = 73.126 (4)^\circ$	$T = 291 \text{ K}$
	$0.28 \times 0.24 \times 0.14 \text{ mm}$

#### Data collection

Bruker SMART CCD area-detector diffractometer	8609 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> in <i>SAINT-NT</i> ; Bruker, 2002)	4295 independent reflections
$T_{\min} = 0.44, T_{\max} = 0.68$	4154 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$

**Table 3**

Selected bond lengths (Å) for (II).

Sm1—O1W	2.4057 (16)	Sm1—O2W	2.4792 (17)
Sm1—O13 <sup>i</sup>	2.4314 (15)	Sm1—O11	2.4956 (15)
Sm1—O12	2.4576 (16)	Sm1—O23	2.5273 (16)
Sm1—O22	2.4695 (17)	Sm1—O13	2.5739 (15)
Sm1—O21	2.4785 (16)		

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

**Table 4**

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

<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>
O1W—H1WB...O11 <sup>i</sup>	0.85 (3)	2.00 (3)	2.823 (2)	165 (2)
N2—H2...N5 <sup>ii</sup>	0.85 (3)	1.54 (3)	2.325 (19)	154 (8)
N2—H2...O6W	0.85 (3)	1.88 (3)	2.640 (17)	149 (7)
N5—H5A...O23 <sup>iii</sup>	0.85 (3)	2.17 (3)	2.96 (2)	154 (6)
N5—H5B...O22	0.85 (3)	2.08 (3)	2.90 (2)	162 (6)
O6W—H6WA...O22 <sup>ii</sup>	0.85 (3)	2.14 (3)	2.82 (2)	137 (7)
O6W—H6WB...O23 <sup>iv</sup>	0.85 (3)	1.97 (3)	2.79 (2)	163 (6)
O1W—H1WA...N1	0.85 (3)	1.88 (3)	2.729 (15)	178 (3)
O1W—H1WA...N3 <sup>ii</sup>	0.85 (3)	2.00 (3)	2.833 (12)	166 (2)
O3W—H3WB...N4 <sup>v</sup>	0.85 (3)	1.93 (3)	2.772 (4)	172 (4)
O2W—H2WA...O4W <sup>vi</sup>	0.85 (3)	2.14 (3)	2.958 (3)	165 (2)
O2W—H2WB...O4W	0.85 (3)	2.00 (3)	2.814 (3)	161 (2)
O3W—H3WA...O11 <sup>i</sup>	0.85 (3)	1.96 (3)	2.808 (3)	174 (4)
O4W—H4WA...O5W	0.85 (3)	1.89 (3)	2.715 (3)	164 (3)
O4W—H4WB...O3W	0.85 (3)	2.06 (3)	2.886 (3)	164 (3)
O5W—H5WB...O12 <sup>iv</sup>	0.85 (3)	2.07 (3)	2.875 (2)	160 (3)
O5W—H5WA...O21 <sup>vi</sup>	0.85 (3)	1.98 (3)	2.815 (2)	170 (3)

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

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.043$	
$S = 1.07$	
4295 reflections	$\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$
365 parameters	$\Delta\rho_{\min} = -0.50 \text{ e } \text{\AA}^{-3}$
22 restraints	

The unbound adenine and one of the solvent water molecules are disordered around an inversion centre into two almost overlapping, equally populated, units.

All the H atoms were clearly seen in a difference Fourier map but were treated differently in the refinement. C-bound H atoms were repositioned at their expected locations and allowed to ride with C—H = 0.93 (alkene) or 0.96 Å (methyl). H atoms attached to N and O atoms were refined with restrained distances of N—H = O—H = 0.85 (1) Å and the water H···H distances were restrained to 1.35 (1) Å. For the methyl H atoms,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , while  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$  for all other H atoms.

The extinction parameters had a significant effect on the refinement and so they were retained, in spite of their small value.

For both compounds, 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: SK3428). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Atria, A. M., Astete, A., Garland, M. T. & Baggio, R. (2009). *Acta Cryst.* **C65**, m411–m414.
- Atria, A. M., Astete, A., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* **E67**, m1191–m1192.
- Atria, A. M., Corsini, G., Herrera, N., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* **C67**, m169–m172.
- Atria, A. M., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* **C67**, m275–m278.
- Atria, A. M., Garland, M. T. & Baggio, R. (2012). *Acta Cryst.* **C68**, m53–m56.
- Atria, A. M., Morel, M., Garland, M. T. & Baggio, R. (2011). *Acta Cryst.* **C67**, m17–m21.
- Benelli, C. & Gatteschi, D. (2002). *Chem. Rev.* **102**, 2369–2388.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2001). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2002). *SAINT* (including *SADABS*). Bruker AXS Inc., Madison, Wisconsin, USA.
- Fujita, M., Kwon, Y.-J., Washizu, S. & Ogura, K. (1994). *J. Am. Chem. Soc.* **116**, 1151–1152.
- Lu, J. Y. & Babb, A. M. (2001). *Inorg. Chem. Commun.* **4**, 716–718.
- Ma, B. Q., Zhang, D. S., Gao, S., Jin, T. Z. & Yan, C. H. (2000). *Angew. Chem. Int. Ed.* **39**, 3644–3646.
- Pan, L., Sander, M. B., Huang, X., Li, J., Smith, M., Bittner, E., Bockrath, B. & Johnson, J. K. (2004). *J. Am. Chem. Soc.* **126**, 1308–1309.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Thompson, L. K. (2002). *Coord. Chem. Rev.* **233–234**, 193–206.
- Wang, R.-H., Hong, M.-C., Su, W.-P., Liang, Y.-C., Cao, R., Zhao, Y.-J. & Weng, J.-B. (2002). *Bull. Chem. Soc. Jpn.* **75**, 725–730.
- Xu, G., Wang, Z. M., He, Z., Lu, Z., Liao, C. S. & Yan, C. H. (2002). *Inorg. Chem.* **41**, 6802–6807.